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Cycling and Control of Metals

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cycling and control of metals

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Marion G. Curry
Gilbert M. Gigliotti

National Environmental Research Center, Cincinnati
February 1973

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PREFACE

This volume is based on a conference held October 31 through November 2, 1972, in Columbus, Ohio. Each of the five sessions of the conference was designed to bring together knowledge and thinking in areas bearing on the problem of metals and their relationship to the environment.

Considering the sources of tracer metals in the environment was only part of the story. Transport and effects, control processes, monitoring for trace metals, and the economic and legal aspects of pollution were also discussed.

The conference was sponsored by the U. S. Environmental Protection Agency's National Environmental Research Center, Cincinnati, National Science Foundation, and the Columbus Laboratories of Battelle Memorial Institute.

We wish to express our gratitude to the many who contributed to the success of the Conference.

Publication of the papers by the U. S. Environmental Protection Agency does not imply endorsement of either the conclusions or any commercial product mentioned in the papers.

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U. S. Environmental Protection Agency

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KEYNOTE REMARKS
METALS: PARTS AND THE WHOLE

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INTRODUCTION

For a few short hours we have come together this week to look at the subject of metals and their relationship to the environment. Metals are an apt subject since they claim the attention of the chemist, physicist, engineer, biologist, physician, statistician, mathematician, economist, and politician. They also pervade the air, the water, and the land. Their deficiencies and overabundances are important to plants, animals, and most importantly, man.

Metals are elements that have a typical luster and that carry a positive charge. The electrolytic chemist defines metals as those substances that are liberated at the cathode. The mining engineer will think of extractable ores; the civil engineer of structural steel. Other recognizable characteristics of metals are their high melting temperatures, low specific heat, good themoelectrical conductivity, hardness, and inability to be deformed permanently without fracture.

Metals and alloys representing mixtures of metals are identified and classified by their chemical, physical, and mechanical properties. Some combination of these three properties usually determines the metal chosen for a specific function. Strength, malleability, and resistance to corrosion are important characteristics of metals in engineering and physical arenas. We all know that gold, silver, platinum, bronze, brass, copper, aluminum, and stainless steel have utility, in addition to certain aesthetic values we appreciate.

We find that the entire plant and animal kingdoms depend on metals in a variety of ways. For example, the blood that flows through our circulation system carrying oxygen to our cells and removing the waste carbon dioxide depends heavily on an atom of iron incorporated into the hemoglobin of the red corpusle. Textbooks on biochemistry or physiology relate that a large group of metals are active within the dynamics of protein anabolism and catabolism. Iron, cobalt, manganese, copper, and magnesium and many other metals are essential to the structure of metalo-proteins. More specifically, the enzymes that catalyze various biochemical reactions within plant and animal systems are often either activated by metals or contain metal.

Although plants and animals need metals, they don't need too much of them. For instance, some scholars implicate an overabundance of lead in the fall of the Roman Empire. The eastern Romans used leaden pots to contain their wine, and they reduced the acidity of wine by adding lead oxide to it. The lead poisoning that followed brought about widespread stillbirths, deformities, and brain damage, particularly among the upper classes who obviously had greater access to lead vessels and to the wine. Some support for this theory comes from the high lead content found in the bones of some ancient Romans. Such accounts, even if speculative, give us some concern over the level of blood lead in the earth's human population, which presently lies between 0.05 and 0.4 parts per million, averaging about 0.25 parts per million. Recent proposals indicate that the toxic threshold level of lead in the blood should be reduced from 0.8 to 0.5 ppm for classical lead poisoning. Despite increased environmental levels, the decrease from earlier high levels is probably resulting from the greater precautions in the use of lead.

Metal deficiencies result in illnesses. In the same way that an overabundant intake of metal results in toxic reactions. The various forms of life on the planet obviously require a variety of metals in various concentrations. We all know now that trace elements are needed in our diets and that we feed our lawns 10 parts of nitrogen, 10 parts of phosphorus, and 10 parts of potassium in the spring. Controlling the intake of metal in our food and water as well as its intake by other animals and plants in the ecological system becomes an important environmental responsibility.

Most of the metal that we use as inhabitants of the earth comes from the crust of the earth. The most important elements, which accounts for about 90% of all the metal used, is iron. The most abundant, accounting for 28%, is silica. Although many metals exist in the earth's crust at quantities of less than one thousandth of a percent, a plentiful supply is related to much of today's pollution. The excess or overabundance that causes toxicity in man and animals can be the cause of pollution on the earth, since abundances, somehow, encourage wastage.

The processes, collectively known as mining, that remove metals from the earth's crust, cause the influx of heavy metals, acid, sediment, and mineralized water, which degraded over 10,000 miles of streams. Approximately 4.5 million acres are disturbed yearly and this number is expected to increase because of the increasing demand for power and metals. After the ore is removed, it must be processed and refined so that the purer form of the metal can ultimately be used to fabricate needed objects and structures. Although the processing and refining operations for the various metals differ widely, these processes have, in the past, contributed greatly to our air pollution, water pollution, and our solid waste problems.

Contrary to popular opinion, concern about the environment has been with us for over six decades. The Federal Government's role in stream pollution control began in 1913 on the northern bank of the Ohio River at Cincinnati. The substantive legislation that implemented broad water pollution control programs was enacted, almost three decades ago, in 1946. Air pollution work began in the 50's. The problems of the management and utilization of wasted solids, which came to the forefront in the 1960's, are present with us in the 70's and promise to claim our attention in the 80's and 90's.

There are certain comfortable personal advantages for the scientist conducting research within the various environmental compartments. Research confined to a narrow avenue can produce sound defensible data, which we need. But this kind of research alone, multiplied by the many scientists who pursue it, may never give us the holistic view of the environment we need to make true progress. I am now convinced that these compartments, air, water, solid waste, pesticide, radiation, noise, etc., cannot be considered independently of one another. The interrelationships between various environmental segments must receive paramount consideration, not only at the level of the research administrator but also by the scientists who conduct research and exchange information in conferences. Man does not live only on a river or only in the air. He is not exposed just to radiation or just to pesticides. Environmental insults occur through all routes: air, water, and food. Man sees it, hears it, feels it, tastes it, and smells it. He inhales it, ingests it, and exposes his skin and mucous membranes to it. He works in it, plays in it, and sleeps in it.

Our task is certainly cut out for us. We have a storehouse of metals present in the earth and available for our use for centuries to come. We must develop a stewardship in the use of these resources that avoids the difficulties of high and low exposures to life forms and encourages reclamation, re-use, and recycling for the ultimate benefit of other generations yet to live on this planet. We must be cautious about the manner in which we mine, process, fabricate, use, and discard these materials. We need a positive plan that will permit the maximum advantage to mankind in the re-use of metallic resources.

Perhaps here in Columbus, we as scientists interested in particular impacts of metals can begin to build a total solution to an environmental problem from our individual data, information, and experience.

SESSION I
SOURCE OF TRACE METALS IN THE ENVIRONMENT

Chairman:

A. W. Breidenbach
U. S. Environmental Protection Agency

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NATURAL SOURCES OF SOME TRACE ELEMENTS IN THE ENVIRONMENT

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INTRODUCTION

Increasing concern over possible hazards to health caused by trace metals, has led to the realization that we need to know much more about their natural and man made sources, their transport under natural conditions, and their entire cycle in the lithosphere, hydrosphere, biosphere, and atmosphere. Since it is necessary to restrict the discussion, data are presented for four elements: lead, cadmium, arsenic, and mercury, in the commonest types of rocks. Emphasis is placed on rocks in which these elements have been concentrated and rocks that are treated by man in ways that the elements might enter the environment in amounts sufficient to affect health.

Average concentrations of these elements in the continental crust, such as those listed in the tables of this paper, represent material generally estimated to consist of about 95% igneous and metamorphic rocks, and about 5% of sedimentary rocks. Detailed estimates of the proportions of various types of igneous and sedimentary rocks have been reviewed (1-3). The distribution patterns of trace elements have been reviewed in several papers in a recent monograph (4).

Igneous rocks, formed by the solidification of melts, constitute most of the continental crust, which is generally considered to be composed mainly of a 2 to 1 ratio of silicic types and basaltic types. The silicic types include the granites and granodiorites that form large plutons such as those of the Sierra Nevada and Idaho batholiths, and also the extrusive rhyolites. Rocks of basaltic type which form the large-scale lava flows of the Columbia and Snake River Basins are the major constituent of the sub-oceanic crust.

The behavior of the trace elements during the formation of the igneous rocks is predictable to a considerable degree from their crystallochemical relations to the major elements of the crystallizing minerals. Nickel and chromium follow magnesium closely and are concentrated in the magnesium-rich ultramafic rocks that are hosts for the major ores of chromium. The minerals of basaltic rocks concentrate: Cu, Zn, and V. Those of granitic rocks concentrate the large cations: K, Ba, Pb, the lanthanides, Zr, U, and Th and the very small ones, Be.

At various stages of igneous processes, by mechanisms that are still in dispute, sulfur-rich fluids separate and form the sulfide deposits. Although these constitute a very small fraction of the Earth's crust, they are the principal ores of Cu, Zn, Pb, Hg, Sb, and Mo, and the major sources of the byproduct trace metals Ag, Cd, Tℓ, In, Ge, and Re.

Rocks at or near the surface of the Earth are subjected to the chemical attack of the atmosphere and ground waters. Water, CO_2, oxygen, and organic compounds are the principal reagents. The reactions are affected by: the composition of the original rocks, pH, the oxidation potential, and the activity of plants, animals, and microbes. The constitutent minerals of the original rocks may be altered to other minerals, or may be dissolved partially or completely, either to precipitate elsewhere, or to be carried to the ocean. The sediments of these minerals are the major scavengers of trace elements on our planet. Fortunately, practically all the trace elements reaching the ocean do not remain in solution, except B, Br, and Se. More than 99 percent are deposited in the oceanic sediments (5, 6).

Although they constitute only 5 percent of the continental crust of the earth, the sedimentary rocks and soil are of far greater importance to man than their magnitude would indicate for two reasons: (a) they constitute a large part of the material exposed at the surface, and (b) they are the materials from which plants and animals derive their food. Shales and clays are the most important sedimentary rocks. Estimates of the relative abundances of the types of sedimentary rocks differ; shales and clays $\leqq 77$ percent, sandstones $\geqq 15$

percent, limestones and dolomites 7.5 to 8 percent (7).

Where the sedimentary rocks are fine-grained, adsorption plays an important role in the concentration of trace elements. In addition, sedimentary rocks which are rich in organic matter, especially the carbonaceous shales, preferentially concentrate many elements, including Hg, As, Mo, Ge, V, and U. The mechanism of concentration is poorly understood, despite its importance (8).

Chemical weathering has produced many of our most important ore deposits. Examples are sedimentary aluminum, iron and manganese oxides, the nickel silicates, and the placer concentrates of minerals that resist breakdown during weathering. The latter are major source of Ti (as rutile and as ilmenite), Zr (as zircon), the lanthanides and Th (as monazite), Au, and the Pt metals. The marine phosphorites, chemical precipitates from the oceans, are notable concentrators of many trace elements, including U, V, the lanthanides, As, Zn, Cd, and Hg (9). Finally, mention must be made of coal and petroleum, the natural transformation products of plant material, in which many trace elements are present.

In the summaries that follow concerning the distribution of lead, cadmium, arsenic, and mercury, particular attention is directed towards concentrations of these elements in natural materials whose present uses (coal, phosphorite, sedimentary iron ores) or possible future uses (oil shale) could cause environmental problems. Data on trace element contents of coal and petroleum are summarized (10), and on black shales (11). All four of these elements are produced commercially from sulfide ores.

Data on concentrations of lead, cadmium, arsenic, and mercury in surface waters of the United States are also summarized. The figures are given for the resultant of the amounts of these elements is the sum of the elements derived from weathering plus those introduced by volcanic emanations plus those introduced into the environment by man's activities.

LEAD

Data on the abundance of lead in natural materials are summarized in Table 1. The element is rather uniformly distributed in these materials, with some degree of concentration in clayey sediments. It is highly concentrated in sulfide deposits.

Data on the concentrations of lead in filtered surface waters of the United States are summarized in Table 2. The amount introduced into the ocean by chemical weathering of rocks is appreciable (6, 10), but is less than the amount of lead emitted to the atmosphere in the United States alone (12), and far less than the annual consumption of lead. It seems safe to estimate that more than 90 percent of the lead discharged into the atmosphere and streams can be ascribed to man-made sources.

TABLE 1 CONCENTRATIONS OF LEAD IN SOME NATURAL MATERIALS, PPM

Type of material	Range usually reported	Average
Continental crust	–	15
Basaltic igneous	2– 18	6
Silicic igneous	6– 30	18
Shales and clays	16– 50	20
Black shales (high C)	7–150	30
Deep sea clays	–	80
Limestones	–	9
Sandstones	< 1– 31	
Soils	1–150	15
Phosphorites	<10–100	10
Coals	2– 50	15

TABLE 2 DISSOLVED LEAD IN SURFACE WATERS OF THE U. S.

(See Reference 13)

Microg/liter (~ ppb Pb)	% of 717 samples
< 1	35.8
1– 4	33.9
5– 9	15.8
10–19	9.8
20–29	2.9
30–79	1.5
> (max. 80)	0.3

CADMIUM

Data on the abundance of cadmium in natural materials are summarized in Table 3; the geochemistry of cadmium has been reviewed (14). Cadmium is a relatively rare element being concentrated in zinc-bearing sulfide ores (ratio Zn/Cd usually 100 to 200) and consequently in all zinc-containing manufactured products.

It is somewhat concentrated in shales and clays and is notably concentrated in phosphorites. Consequently, it is present in manufactured phosphate fertilizers.

Most fresh waters contain less than 1 ppb Cd. The chemistry of cadmium and zinc in surface and ground waters has been reviewed recently (15), giving calculations of equilibrium solubilities with the hydroxide or carbonate as solid phase. Most waters were unsaturated with respect to these phases. About 20 percent had cadmium contents in reasonable agreement with solubilities calculated assuming $CdCO_3$ as equilibrium solid phase. Analyses of sea water average about 0.15 microg/l. (~ppb).

TABLE 3 CONCENTRATIONS OF CADMIUM IN SOME NATURAL MATERIALS, PPM

Type of material	Range usually reported	Average
Continental crust	–	0.2
Basaltic igneous	0.006– 0.6	0.2
Silicic igneous	0.003– 0.18	0.15
Shales and clays	0 – 11	1.4
Black shales (high C)	0.5 – 8.4	2.0
Deep sea clays	0.1 – 1	0.5
Limestones	–	0.05
Sandstones	–	0.05
Soils	0.1 – 0.5*	0.3*
Phosphorites	0 –170	30
Coals	–	2

*Excluding soils from mineralized areas.

Table 4 summarizes data on surface waters of the United States. Concentrations above natural background are almost certainly due to industrial waste. Even higher concentrations (up to 450 ppb Cd) have been reported in the South Fork of the Coeur d'Alene River in Idaho (16), a stream that drains an area containing extensive dumps of ground mill tailings from Pb-Ag-Zn ores.

As with lead, it seems safe to estimate that more than 90 percent of the cadmium discharged to the atmosphere and streams in the environment can be ascribed to man-made sources.

ARSENIC

Data on the concentrations of arsenic in natural materials, recently reviewed (17), are summarized in Table 5. Arsenic is especially concentrated in sulfide ores, predominantly as arsenopyrite (FeAsS), but also as a constituent of many complex sulfides of copper and lead, such as enargite and tennantite. Arsenic is concentrated in shales, clays, phosphorites, coals, sedimentary iron, and manganese ores. Industrial processes using these materials supply considerable amounts of arsenic to the atmosphere and to surface waters. Another possible source is petroleum. Recent analyses show 0.005 to 1.1 (median 0.09) ppm As, but there are few analyses.

TABLE 4 CADMIUM IN FILTERED SURFACE WATERS OF THE U. S.

(See Reference 13)

Microg/liter (~ ppb Cd)	% of 727 samples
< 1	54.2
1– 4	32.3
5– 9	7.7
USPH upper limit	
10– 20	4.1
21– 40	0.9
41–130	0.8
	100.0

TABLE 5 CONCENTRATIONS OF ARSENIC IN SOME NATURAL MATERIALS, PPM

Type of material	Range usually reported	Average
Continental crust	–	2.0
Basaltic igneous	0.2– 10	2.0
Silicic igneous	0.2– 13.8	2.0
Shales and clays	–	10.
Deep sea clays	–	13.
Limestones	0.1– 8.1	1.7
Sandstones	0.6– 9.7	2
Soils	0 – 102.*	5*
Phosphorites	0.4–2000	13
Sedimentary Fe ores	70 –1100	400
Sedimentary Mn ores	up to 1.5%	–

*Excluding soils from mineralized ares

Most of the arsenic in non-marine shales is associated with the clay minerals, whereas in offshore marine samples a considerable proportion of the arsenic is present in pyrite FeS_2 (18). The arsenic in coal may also be present in pyrite. Strong positive correlation between the contents of arsenic and of organic carbon have been found for the Pierre Shale (19), and for unconsolidated sediments of Lake Michigan (20). The latter had much higher arsenic contents in the near-surface sediments (0 to 6 cm.) than in those at depths greater than 20 cm. (12.4 vs. 5.3 ppm). This indicates a recent increase in the proportion due to man's activities.

In the manufacture of superphosphate fertilizer by treatment of phosphorite with sulfuric acid, most of the arsenic present in the phosphorite passes into the manufactured fertilizer. If the sulfuric acid used is made from sulfide ores, it is likely to contain considerable arsenic. Superphosphate made in this way has been reported to contain up to 0.1 percent As.

Data on filtered surface waters of the United States are summarized in Table 6. The concentrations of arsenic are evidently due, in part, to industrial contamination, and probably, in part, to urban wastes such as high-phosphate detergents (21). It should be noted that fumarolic gases associated with volcanism have been reported to contain up to 0.7 ppm As and that waters of hot springs contain up to 13.7 ppm As. Most ground waters are low in arsenic, averaging perhaps 1 ppb As, but concentrations high enough to endanger health (22), have been reported often enough to warrant concern.

TABLE 6 DISSOLVED ARSENIC IN FILTERED SURFACE WATERS OF THE U. S.

(See Reference 13)

Microg/liter (~ ppb As)	% of 728 samples
< 10	76.8
10– 19	15.8
20– 29	3.5
30– 49	2.5
——— USPHS upper limit ———	
50– 99	1.1
100–1100	0.3
	100.0

Although quantitive data is lacking, it has been suggested that microbial action, under highly reducing natural conditions, might lead to the formation of arsine or other volatile arsenic compounds.

Although data are insufficient for an estimate of magnitude, it seems probable that the natural sources mentioned, including the erosion of surface rocks, may account for a significant portion of the discharge of arsenic to the atmosphere and streams.

MERCURY

Recent concern over the health hazards of mercury has triggered much research on its geochemistry, including the appearance of reviews (23–25). Nevertheless, the average abundances listed in Table 7 are much more uncertain than those for the elements previously discussed. This is due in part because of the difficulty of analysis for such low concentrations, and because of the uncertainty caused by the very high concentrations reported in some areas of the world (23). Some of the estimates in Table 7, especially those for shales, deep sea clays, and coals are higher than previous estimates and may still be too low, on shales, (26); on river, lake, and ocean sediments (27–35). The cycle of mercury in the environment has been reviewed (36).

TABLE 7 CONCENTRATIONS OF MERCURY IN SOME NATURAL MATERIALS, PPM

Type of material	Range usually reported	Average
Continental crust	--	0.06
Basaltic igneous	0.002– 0.5 *	0.05 *
Silicic igneous	0.005– 0.4 *	0.06 *
Shales and clays	0.005– 1.0 *	0.16 *
Black shales (high C)	0.03 – 2.8	0.5
Deep sea clays	0.02 – 2.0	0.4
Limestones	0.01 -- 0.22*	0.04 *
Sandstones	0.001– 0.3 *	0.05 *
Soils	0.001– 0.5 †	0.05 †
Phosphorites	0.001– 0.95	0.050
Coals	0.05 –13.3 *	0.3 *

*Not including many analyses, especially from the Donets Basin, Kerch-Taman area, and Crimea, USSR, that show contents 10–1000 times the average given.

†Excluding soils from mineralized areas

Mercury is concentrated in sulfide ores, especially those of zinc and to a lesser extent in those of copper. The determination of mercury has been widely used as a tool in geochemical prospecting for such ore deposits. It is notably concentrated in shales and clays, especially those rich in organic matter, in some phosphorites, and in coal (20, 37–40). Up to 2.9 ppm Hg has been reported in petroleum, but there are too few analyses to permit an estimate of the environmental impact.

Mercury can reach the environment from all these sources, either by the action of chemical weathering or during industrial processing. Mercury differs from the other elements in two important respects. First, its vapor pressure, even at surface temperatures, is so high that direct volatilization to the atmosphere is significant (see Table 9). A very high proportion of the mercury present in coal is volatilized during burning. Second, it is now well established that the mercury in fluvial and lacustrine sediments can be converted, by microbial action, into organic mercury compounds (methyl mercury). These compounds are partly volatilized and partly taken up by living matter, especially fish; reintroducing them to the environment.

Data on the concentrations of mercury in filtered surface waters of the U.S. are summarized in Table 8. The available evidence indicates that most of the mercury reaching streams, lakes, and the ocean is precipitated rapidly.

Mercury is a constituent of volcanic emanations (Table 9) and of fumarolic vapors and hot springs associated with volcanic emanations. Although data are insufficient

TABLE 8 DISSOLVED Hg IN FILTERED SURFACE WATERS OF THE U. S.

(See References 13 and 41)

Microg/liter (~ ppb Hg)	% of 706 samples
< 0.5	52.1
0.1– 0.4	21.8
0.5– 2.0	15.7
2.0– 4.9	5.8
——— EPA upper limit ———	
5.0– 9.9	2.0
11.0–19.9	1.6
> 20 (max. 740)	1.0
	100.0

TABLE 9 MERCURY IN AIR AND IN VOLCANIC EMANATIONS, (IN NANOGRAMS PER CUBIC METER) (1 NANOGRAM=10^{-9} g.)

Sample	Range	Average
AIR		
Over Pacific Ocean, 20 miles offshore	0.6–0.7	–
Arizona and Calif., unmineralized areas	3–9	5
California	1–50	–
Chicago area	3–39	9.7
Moscow and Tula regions, USSR	80–300	–
400 ft. above porphyry copper deposits, USA	7–53	27
400 ft. above mercury deposits, USA	24–108	60
Over mercury deposit, USSR	200–1200	–
AIR and GASES, volcanic regions		
Air, Kamchatka region, USSR	–	190
Air, Honolulu, Hawaii	40–910*	–
Air, Sulfur Banks, Kilauea Volcano	21,400–23,300*	–
Air, vent breccias of mud volcanoes USSR	300–700	–
Gases, mud volcanoes USSR	700–2000	–
Gases, Mendeleev, and Sheveluch Volcanoes, USSR	300–4000	–
Gases from hot springs, Kamchatka and Kuriles	10,000–18,000	–

*Data source reference 42.

to permit quantitative estimates, the very large amount of material involved, especially the emanations from mud volcanoes, indicates the proportion of mercury reaching the atmosphere and waters from natural sources must be high; possible of the order of 30 to 70 percent of the total.

A recent study (27) (see Figure 1) gives data on the mercury contents of a drill core taken from the sediments of southeastern Lake Ontario, which show a spectacular increase of mercury from 1906 to the 1940's. From these data, the present daily input of mercury into Lake Ontario is estimated to be 42 lb. (19 kg.) Hg from natural sources and 83 lb (37.6 kg) from industrial sources (27). In this industrialized area, man's activities supply about two-thirds of the mercury.

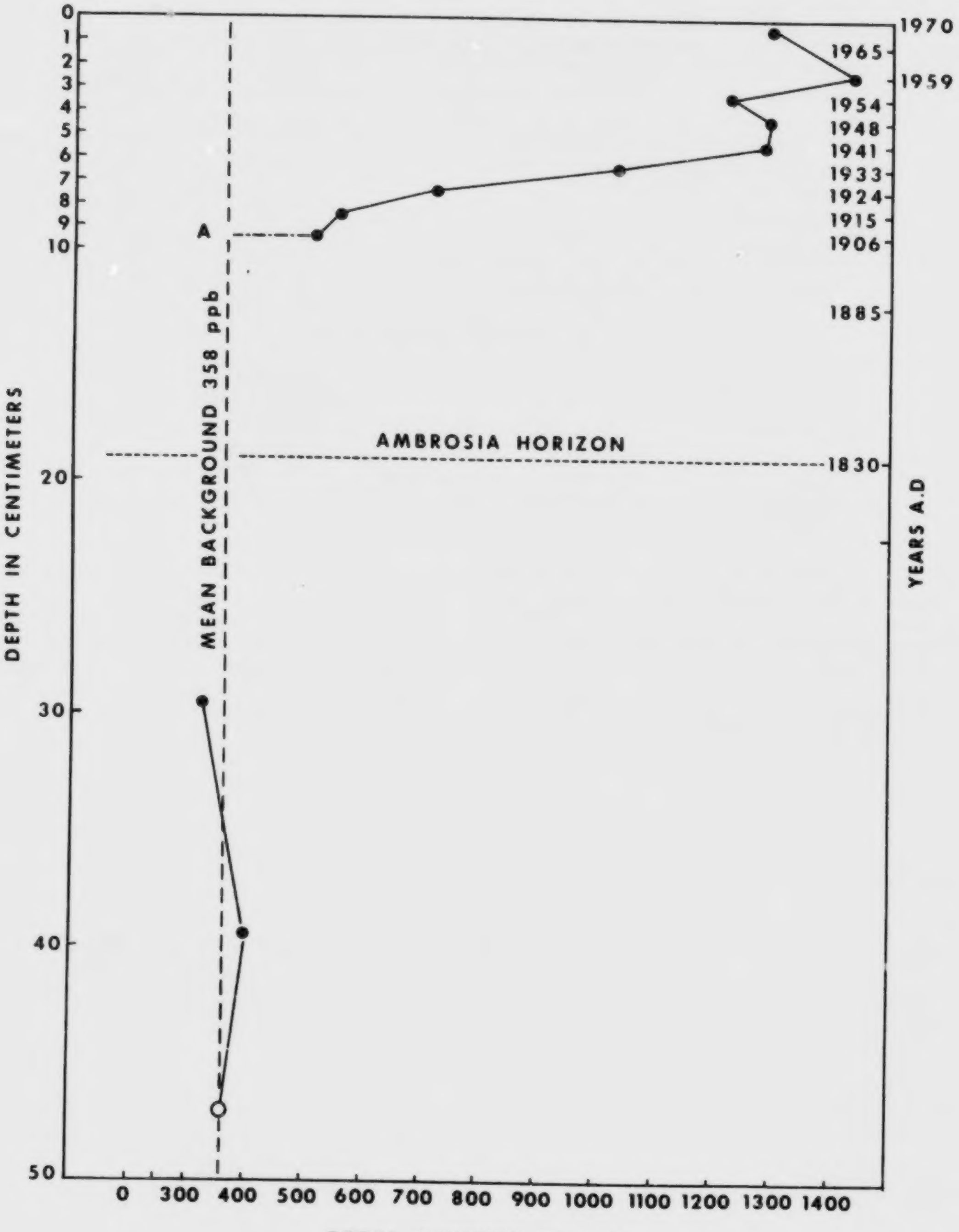

Figure 1. The vertical distribution of total observed mercury in core E30, expressed in ppb.

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THE LEAD INDUSTRY AS A SOURCE OF TRACE METALS IN THE ENVIRONMENT

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INTRODUCTION

During the past five years the world's most modern lead industry has developed in a remote Ozark's section of Southeastern Missouri. The economical impact of this vast mineral resource is just starting to be known and promises to offset predictions that sufficient mineral reserves still must be discovered in order to meet lead demands during the balance of this century (1). The third annual report of the council on environmental quality (2) emphasized that the low-cost lead producers in Missouri would be able to maintain peak production and be able to absorb pollution control costs while high-cost lead producers in other states may be unable to raise the required capital for pollution control and be forced to close.

In 1970 the Viburnum Trend or New Lead Belt ranked first in the world by producing 432,576 tons of lead ore (3), and in 1971 continued to pace the United States in lead production (4). Present production trends for the period January through July 1972 indicate that 289,073 tons of lead have been recovered, which is 46,000 tons above the same period in 1971 (5). This rapid industrial development in a sparsely populated rural forest region has resulted in the release of lead, copper, zinc, cadmium, and other trace metals into a formerly unaffected ecosystem. Due to this abrupt change, the mining district has become a unique area for studying the impact of trace metals and developing techniques to control detrimental effects. Pollution abatement studies have been conducted since 1967 and during the past 18 months an interdisciplinary team, supported by the National Science Foundation RANN Lead Study Program with the assistance of local citizens, the mining industry, concerned local, state, and Federal agencies, have conducted an extensive investigation on the environmental effects of this industrial development. A complete report of this investigation has been published as an interim progress report to National Science Foundation (6).

Research has been carried out to determine background values, to establish natural baselines (7, 8) and to evaluate the lead industry as a source of trace metals in the environment. The unusual topography and drainage pattern of the mining area assisted, since it was possible to study control sites on streams in the same area that were not affected by industrial development. By further use of selected sites below individual mine-mill operations, wastewater effects on receiving streams could be studied. The location of the New Lead Belt, the unique stream drainage pattern, mines and mills, settling lagoons, a lead smelter, and stream sampling sites are shown in Figure 1.

Sources of trace metals in the environment were associated with: symbol A, the mining and milling operations with problems of grinding, concentrating and transporting ores, and disposal of tails along with mine and mill wastewater; and symbol B, the smelter-refinery process with problems of concentrate haulage, storage, sintering, refining, atmospheric discharges, and blowing dust. The systematic exchange and transport from these operations are illustrated in Figure 2 which depicts the possible sources of trace metals in the environment of the New Lead Belt of Southeastern Missouri.

MINING AND MILLING SOURCES

Efficient and modern engineering designs have been incorporated into the mines and mills within the New Lead Belt. Galena (lead) is the principal ore mined with lesser quantities of sphalerite (zinc), chalcopyrite (copper), and silver recovered as economic co-products. Geologically the lead ore is disseminated throughout the Cambrian Bonneterre Formation, mostly a dolomite, at depths ranging from 700 to 1,200 feet. Since the producing formation also serves as a good aquifer, most mines must employ constant pumping, ranging from 3,000 to 7,000 gpm, in order to prevent flooding. This inflow of water has reduced mine dust as a potential problem source but the mine water pumped to the

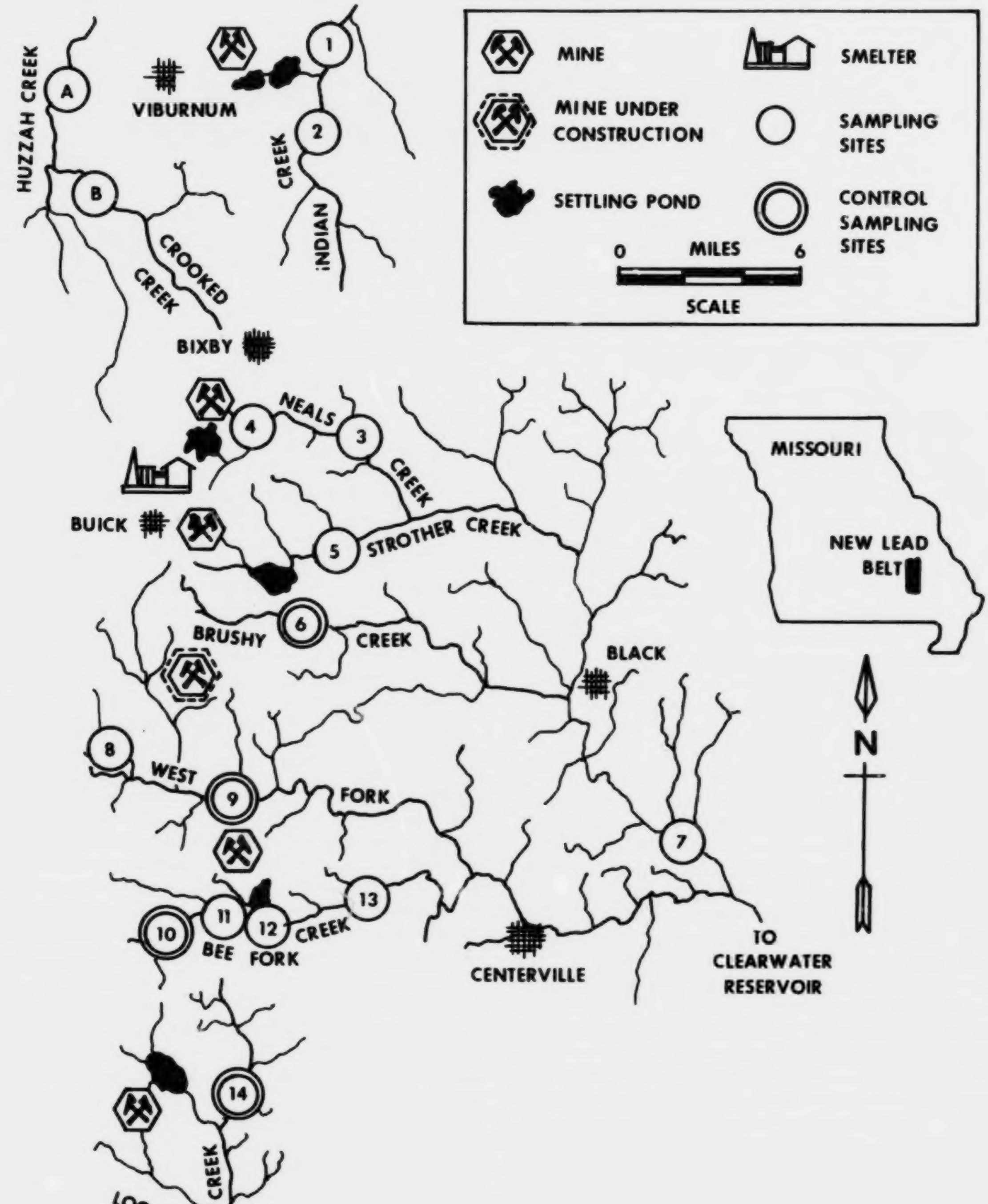
MINE
SMELTER
MINE UNDER CONSTRUCTION
SAMPLING SITES
SETTLING POND
CONTROL SAMPLING SITES
0 MILES 6
SCALE
HUZZAH CREEK
A
B
VIBURNUM
1
2
CREEK
INDIAN
CROOKED CREEK
BIXBY
NEALS CREEK
3
4
BUICK
5
STROTHER CREEK
6
BRUSHY CREEK
BLACK
MISSOURI
NEW LEAD BELT
N
8
WEST FORK
9
7
13
10
11
12
BEE FORK CREEK
CENTERVILLE
TO CLEARWATER RESERVOIR
14
LOGAN CREEK
15

Figure 1. The New Lead Belt of southern Missouri.

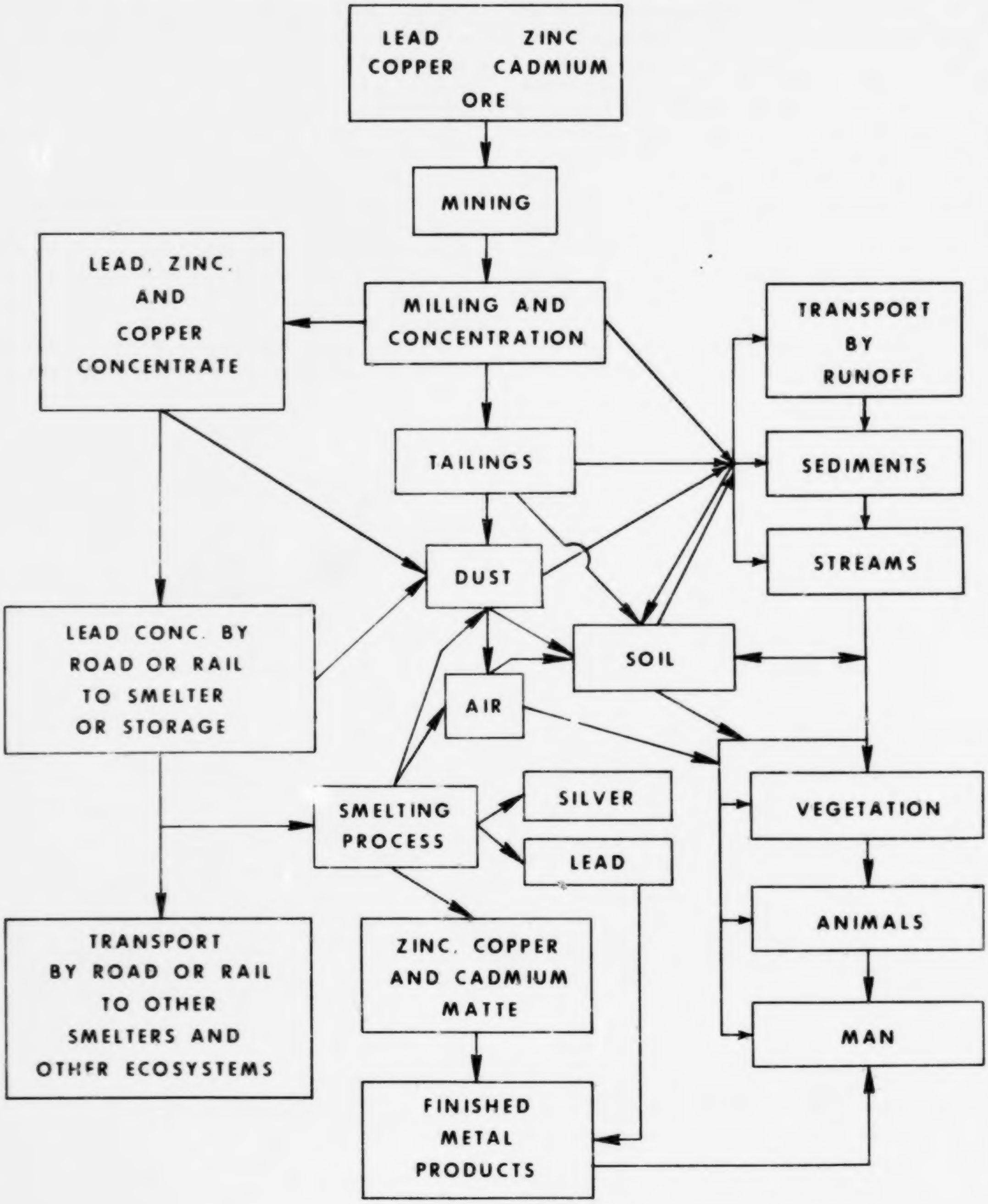
LEAD ZINC
COPPER CADMIUM
ORE
MINING
LEAD, ZINC, AND COPPER CONCENTRATE
MILLING AND CONCENTRATION
TRANSPORT BY RUNOFF
TAILINGS
SEDIMENTS
STREAMS
DUST
LEAD CONC. BY ROAD OR RAIL TO SMELTER OR STORAGE
SOIL
AIR
VEGETATION
SMELTING PROCESS
SILVER
LEAD
ANIMALS
TRANSPORT BY ROAD OR RAIL TO OTHER SMELTERS AND OTHER ECOSYSTEMS
ZINC, COPPER AND CADMIUM MATTE
MAN
FINISHED METAL PRODUCTS

Figure 2. Sources of trace metals in the environment of the New Lead Belt of Southeastern Missouri.

surface does contain an appreciable amount of fine galena and associated trace metals as well as associated spillage from equipment operations and maintenance.

Generally mines in the new mining district are worked by a standard room-and-pillar method. The back ore is drilled and shot in one or two passes followed by haulage to a gyratory crusher via large diesel loaders or locomotive-drawn railcars. After primary crushing underground, the ore is hoisted to the surface in a skip. Most of the mines also employ two shafts, one for men and equipment and one for ore hoisting and charging of the ore bin at the mill. Since automation is a key factor, the best known equipment and technology is employed at the mines.

Part of the water pumped from the mines is utilized as a process water, for the milling procedure, where chemical reagents are added during the flotation circuit to separate the lead, zinc or copper minerals from the finely ground rock or gangue. The flotation reagents usually consist of chemical collectors, frothers, depressants, and activants.

The lead and zinc, and sometimes copper, minerals from the flotation process are pumped into thickeners, where the concentrate settles leaving the water, excess flotation reagents, colloidal, and supracolloidal minerals to be discharged as a milling effluent. The concentrate is vacuum dried by various methods and then transported to smelters for the final conversion of metal. A typical mine and mill production flow chart is illustrated in Figure 3.

The water and tailing wastes from the mine and mill operations are discharged into settlement and treatment

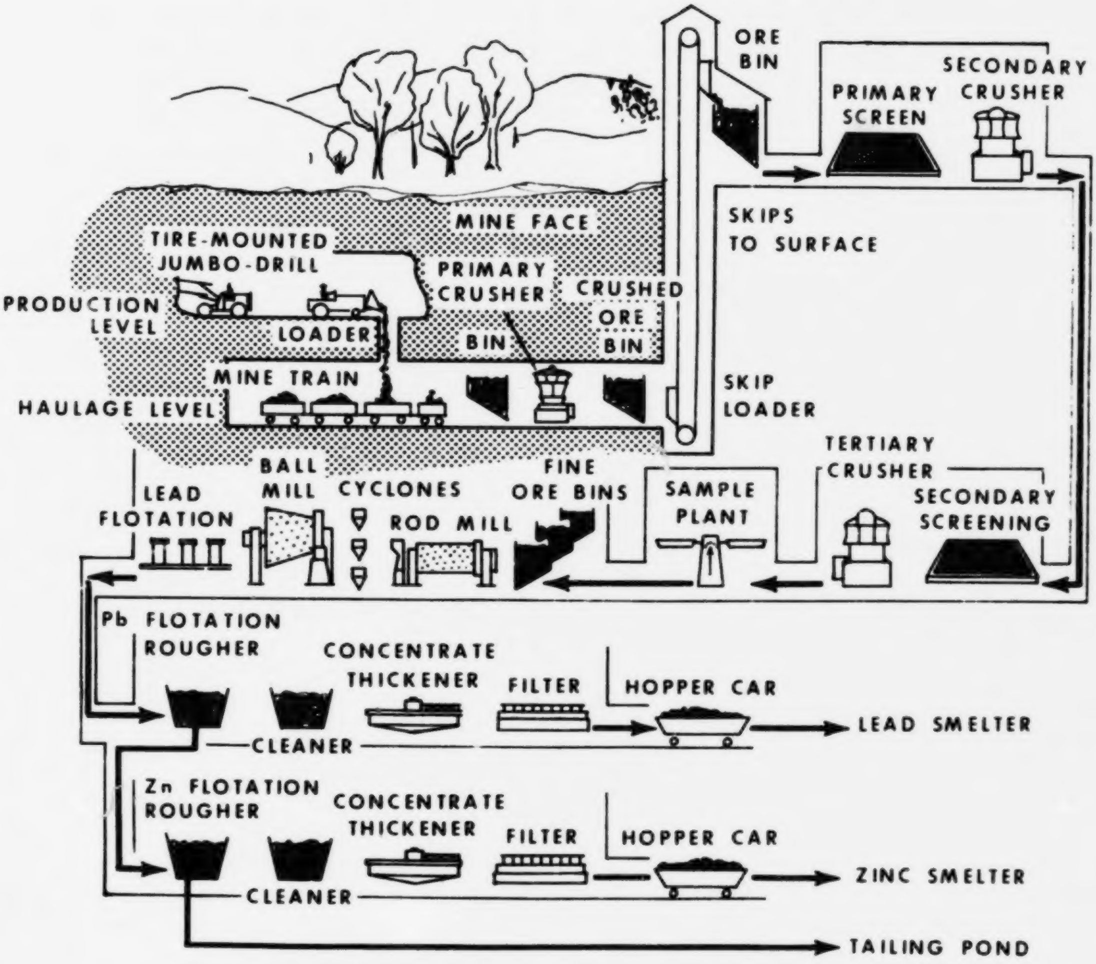
ORE BIN
SECONDARY CRUSHER
PRIMARY SCREEN
MINE FACE
SKIPS TO SURFACE
TIRE-MOUNTED JUMBO-DRILL
PRIMARY CRUSHER
CRUSHED ORE BIN
PRODUCTION LEVEL
LOADER
BIN
MINE TRAIN
SKIP LOADER
HAULAGE LEVEL
TERTIARY CRUSHER
BALL MILL
FINE ORE BINS
SAMPLE PLANT
SECONDARY SCREENING
LEAD FLOTATION
CYCLONES
ROD MILL
Pb FLOTATION ROUGHER
CONCENTRATE THICKENER
FILTER
HOPPER CAR
LEAD SMELTER
CLEANER
Zn FLOTATION ROUGHER
CONCENTRATE THICKENER
FILTER
HOPPER CAR
ZINC SMELTER
CLEANER
TAILING POND

Figure 3. Mine-mill production flow chart. [Courtesy of Amax Lead Co. of Mo.]

lagoons. The tailing pond dams are usually constructed from the tails, generally less than 200 mesh in size, of the ore concentration process which are separated into fine and coarse fractions by cyclones, centrifugal separators. Once the dams have been initially constructed, the tailings and other liquid wastes are introduced upsteam until the lagoon is effectively filled. The lagoons are supposed to settle out residual tails and biologically degrade any spent organic reagents discharged from the milling process.

In order to evaluate the effects of the developing lead mines on water quality and aquatic ecosystems, an extensive sampling program was established. Twenty-one principal sampling sites were selected. Samples were bi-monthly and analyzed for both heavy metals and organic parameters of pollution.

Quantitative determinations of the dissolved and suspended metallic content of the water, algae, stream sediments, and aquatic biological specimens were determined using atomic absorption techniques. Basic water quality measurements, other than metals, were performed (9).

Visual observations were made of the general stream conditions, amount of flow, dominant plant life, and apparent animal life. Preliminary studies were conducted to ascertain heavy metals concentrations in algal mats and other aquatic vegetation at selected areas both upstream and downstream from selected sites where contamination was indicated.

Heavy metal concentrations in the streams, before the start of the mining activity and in the control streams following the start of the activity, were found to be in the range of 1 to 20 parts per billion (ppb) for copper, lead, and zinc. Most of the values were in the 4 to 6 ppb range and the water pH ranged from 7.0 to 8.8 (10). Other geochemical background values were 1.5 to 27 ppm for calcium, 0.8 to 5 ppm for sodium, 0.5 to 0.9 ppm for potassium, and up to 30 ppb for manganese.

The results of lead analyses on selected stream sites, over a one year period, showed 22 separate unfiltered samples which were in excess of the 0.05 ppm limit set for drinking water by the U. S. Public Health Service (11). Six of these samples, of which the highest contained 0.83 lead, occurred on the same day, December 15, 1971. These high values were invariably concomitant with storm runoff, and the stream flow during the storm of December 15 was of sufficient quantity and turbulence to achieve complete scouring of the bottom with virtually complete removal of the biological slime layer on all affected streams.

There were some 42 episodes noted where the zinc concentrations were above the 0.1 ppm established as the maximum allowable concentration in the Effluent Guidelines proposed by the Missouri Clean Water Commission. The highest value (0.237 ppm) was observed on December 15, concomitant with heavy runoff. Results therefore indicate that problems with zinc in effluents occur in two mining and milling effluent discharges.

There were 11 episodes of copper concentrations in excess of the 0.02 ppm guidelines set by the Missouri Clean Water Commission and the U. S. Public Health Service standards for fish toxicity.

Further investigations indicated that the heavy metal content of mine and mill discharge waters, in the New Lead Belt of Southeastern Missouri, could be sufficiently reduced in retention lagoons to permit discharge into streams (7). Under existing geochemical conditions, slightly basic pH and elevated bicarbonate content, excess heavy metals are probably precipitated as carbonates.

Samples of algal mats, biological slimes, and aquatic vegetation were collected for analysis of heavy metals contamination and found that heavy metals concentrations were highest, approximately 8000 ppm on a dry weight basis, near the tailings dams of milling operations (12). The dense and tangled communities of algae and associated microconsumers were found to act as excellent filters in addition to their nutrient trapping and recycling abilities. The finely ground particles of rock flour or minerals, that escaped the flotation process and tailings reservoirs, are efficiently trapped and removed by the benthic flora. Figure 4 illustrates the accumulation of trace metals in algae on streams receiving mine and mill effluent.

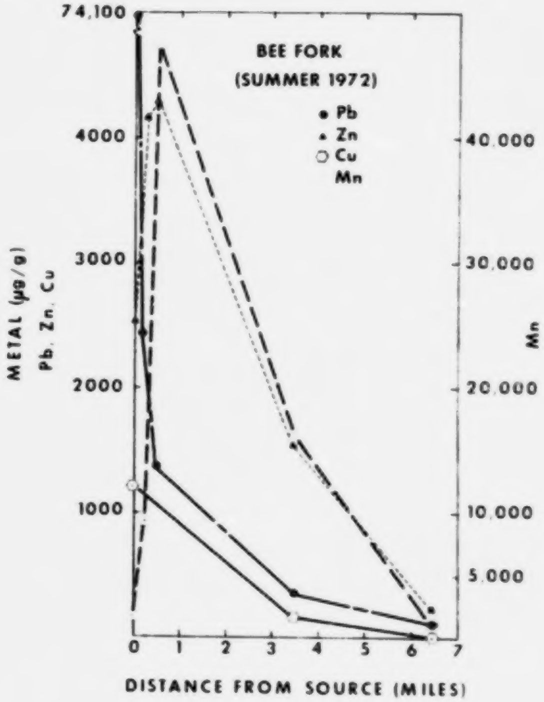

Figure 4. Heavy metals concentration in algae.

Regardless of the aquatic plant species tested, the concentration of heavy metals was most prolific on those samples collected near the source of heavy metals at the tailings ponds. The exact nature of the association of the heavy metals with the algae or other plant life remains to be established. Additional work has been carried out on some stream consumer organisms such as tadpoles, crayfish, snails, minnows, and larger fishes, but evaluations are incomplete at this time.

Using these data and input from the many other research areas involved in this study, a number of recommendations have been made or implemented by the mining companies, including:

A. Dust containing heavy metals from the tailings dams is suspect as a source of stream pollution and these dams should be covered with soil and planted with grass to prevent future problems.

B. The lagoons used to treat the milling wastes have been redesigned to prevent short circuiting, thereby allowing better sedimentation and biodegradation of the organic reagents used. Where economically possible, total recirculation of the mill water has been advised. Figure 5 illustrates the modified mining and milling lagoon waste treatment scheme now employed at one mine as opposed to their prior normal mining and milling wastewater ponding scheme (13).

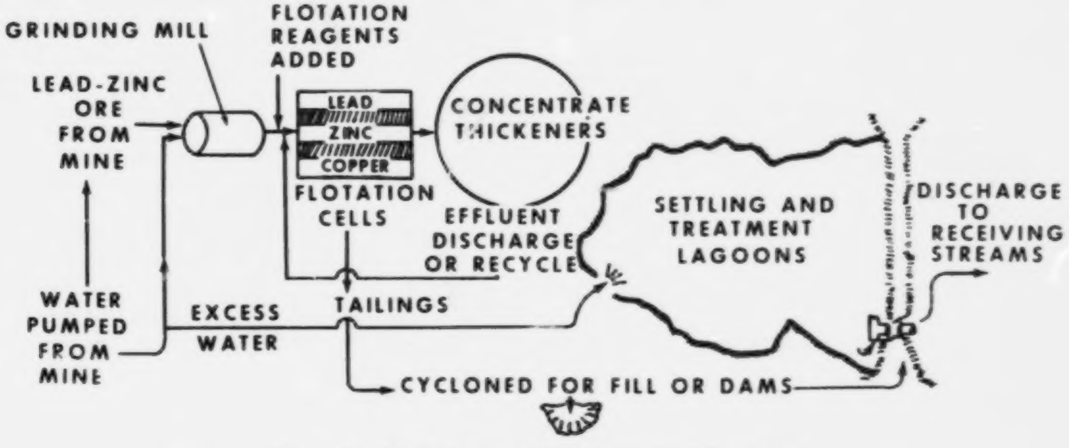
GRINDING MILL
FLOTATION REAGENTS ADDED
LEAD-ZINC ORE FROM MINE
LEAD
ZINC
COPPER
FLOTATION CELLS
CONCENTRATE THICKENERS
SETTLING AND TREATMENT LAGOONS
DISCHARGE TO RECEIVING STREAMS
EFFLUENT DISCHARGE OR RECYCLE
WATER PUMPED FROM MINE
EXCESS WATER
TAILINGS
CYCLONED FOR FILL OR DAMS

Figure 5a. Flow diagram of mining and milling wastes.

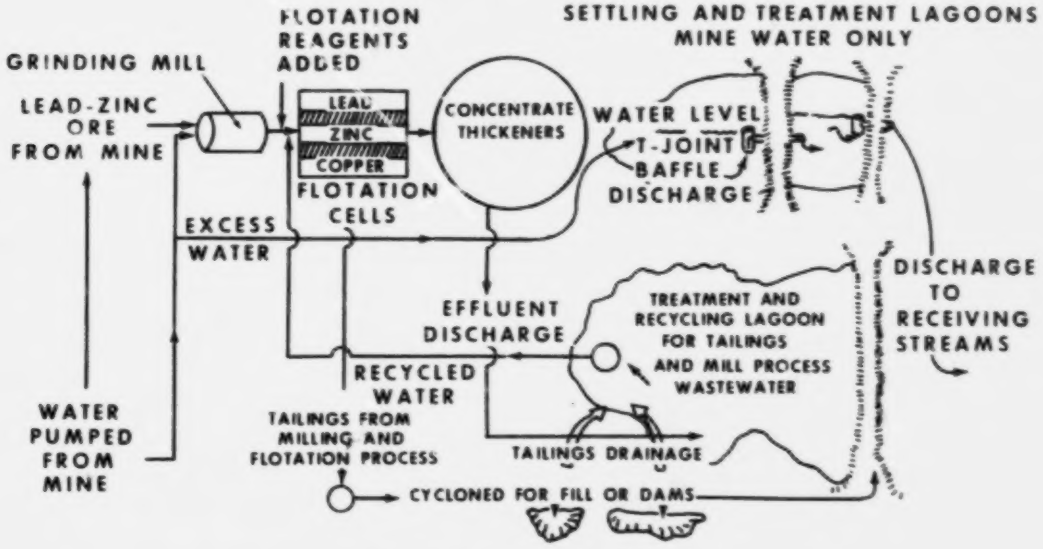
FLOTATION REAGENTS ADDED
SETTLING AND TREATMENT LAGOONS MINE WATER ONLY
GRINDING MILL
LEAD-ZINC ORE FROM MINE
LEAD
ZINC
COPPER
CONCENTRATE THICKENERS
WATER LEVEL
T-JOINT
BAFFLE
DISCHARGE
FLOTATION CELLS
EXCESS WATER
DISCHARGE TO RECEIVING STREAMS
EFFLUENT DISCHARGE
TREATMENT AND RECYCLING LAGOON FOR TAILINGS AND MILL PROCESS WASTEWATER
RECYCLED WATER
WATER PUMPED FROM MINE
TAILINGS FROM MILLING AND FLOTATION PROCESS
TAILINGS DRAINAGE
CYCLONED FOR FILL OR DAMS

Figure 5b. Modified flow diagram for treatment and recycling of mining and milling wastes.

TRANSPORTATION SOURCES

The effects of railroad and truck transportation of lead, zinc, and copper concentrate has also been studied. The railroad, which dissects the smelter area in a north-south direction, is used for transporting supplies to the industries and for carrying out finished lead metal or ore concentrates in gondola cars which are open at the top. The influence of this ore concentrate haulage by truck and railroad has been evaluated and elevated levels of trace metals have been found at distances of up to 100 feet from the road (6). Plants used in this study were tall fescue, a domesticated forage grass, purple top, a native grass species, and blueberry. Values of 4000 ug/g (dry weight) were found for purple top at roadsides along ore haulage routes, as compared with 49 ug/g (dry weight) found along nonhaulage control routes.

Concurrent work was carried out on soil samples taken from traverses at right angles to haulage routes (6). Data also indicated that the transport of ore concentrate in open trucks or railroad cars, without coverage, contributes windblown trace metals into the environment. Additional research work is being continued to evaluate amounts and rates of materials and possible control measures.

SMELTER AREA SOURCES

The industrial operations in the smelter area involve smelting sinter in the blast furnace to produce finished lead. The metallic impurities associated with the production of lead are copper, silver, zinc, and cadmium. The air pollution problems created by smelting the sulfide-containing concentrates include sulfur dioxide derived from sinter machines; as well as dusts, and fumes containing lead and other heavy metals from the sintering operation.

The smelter complex converts galena ore to usable metal. Lead concentrates, containing 65 to 75 percent lead and 14 to 17 percent sulfur, are brought to the plant by rail and trucks. Concentrates are mixed with fluxing materials, such as silica and limestone, along with granulated slag and delivered to the sintering plant, where the mixture is roasted, to burn off the sulfur, and converted to a porous material called sinter. The resulting sinter is combined with coke and charged into the top of a blast furnace. The charge is ignited in a high oxygen environment, melted, and reacted to form molten lead and slag. Lead and slag flow from the furnace into a brick-lined settler. Slag overflows the settler into a granulation pit, where it is transferred to storage. Lead bullion is tapped into pots and transferred to drossing kettles where it is refined and cast into either 100 lb pigs or 1-ton ingots. A typical general flow sheet of lead smelting is shown in Figure 6.

During normal production 450 tons of concentrates are charged to the furnaces per day; the smelter under

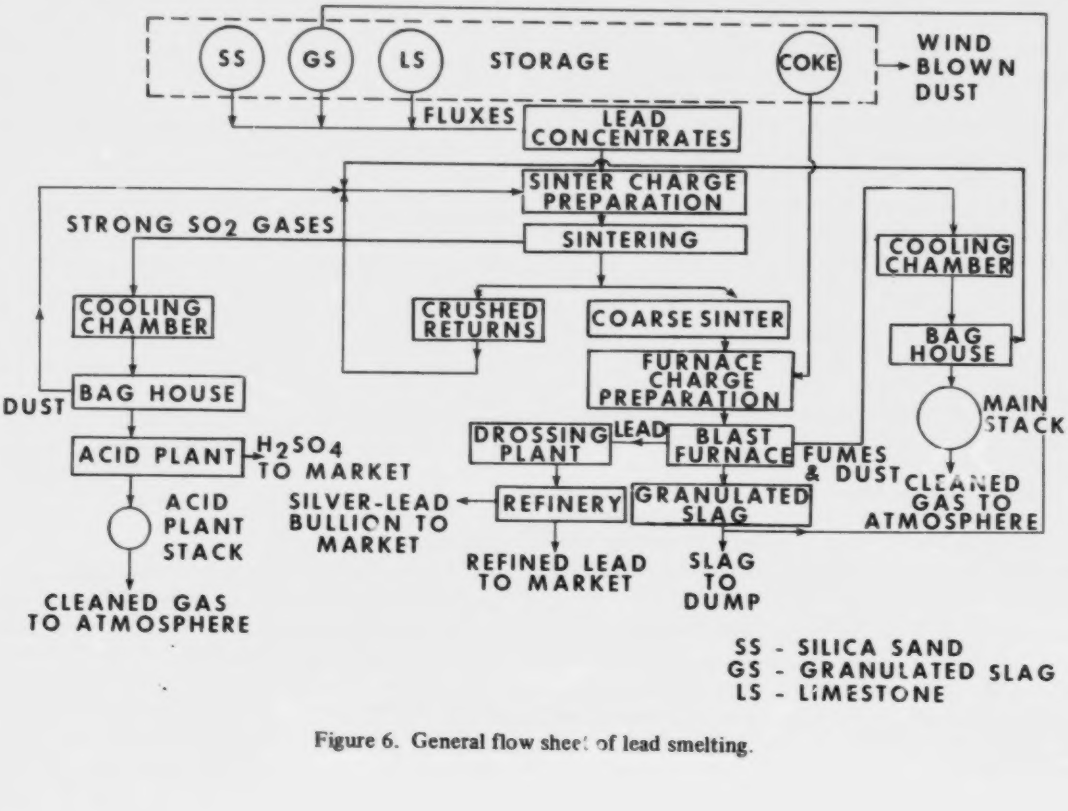
SS
GS
LS
STORAGE
COKE
WIND BLOWN DUST
FLUXES
LEAD CONCENTRATES
SINTER CHARGE PREPARATION
STRONG SO2 GASES
SINTERING
COOLING CHAMBER
CRUSHED RETURNS
COARSE SINTER
COOLING CHAMBER
BAG HOUSE
FURNACE CHARGE PREPARATION
DUST
BAG HOUSE
MAIN STACK
DROSSING PLANT
LEAD
BLAST FURNACE
ACID PLANT
H2SO4 TO MARKET
FUMES & DUST
CLEANED GAS TO ATMOSPHERE
ACID PLANT STACK
SILVER-LEAD BULLION TO MARKET
REFINERY
GRANULATED SLAG
REFINED LEAD TO MARKET
SLAG TO DUMP
CLEANED GAS TO ATMOSPHERE
SS - SILICA SAND
GS - GRANULATED SLAG
LS - LIMESTONE

Figure 6. General flow sheet of lead smelting.

these conditions emits 30 to 75 tons sulfur dioxide through a 200-ft stack when sinter plant, sulfuric acid recovery plant, and blast furnace are operating. This particular lead industry has annually contributed approximately 11,000 to 27,400 tons of sulfur dioxide and about 100 to 200 tons of particulate matter depending upon the operation condition of the plant.

Research studies have been conducted with three sulfur dioxide monitoring stations, 10 dustfall stations and two meteorological stations. Sulfur dioxide was continuously monitored. Settleable particulates were collected once a month, and wind direction and speed were monitored continuously.

The settleable particulate samples were analyzed for four metals, cadmium, copper, lead, and zinc by the atomic absorption technique and the results were reported as grams per square meter per month (g/m^2-month).

The maximum values of deposition rates of particulate lead have occurred at sampling stations which were located near the railroad, even though the most frequent wind direction was not always toward these stations (14). This indicates the influence of the open railroad cars and the prevailing winds around the vicinity of the stations. The annual average of settleable particulate lead, for the ten sampling sites, is illustrated in Figure 7.

The particulate lead was found to be as high as 20.5 g/m^2 per month at station 7 with an annual average of 8.6 g/m^2 per month. Normally, three locations (stations 3, 6, and 7) within a distance of 1000 ft from the stack showed high deposition rates as compared to other stations. This indicated that the metallic particulates do not travel far from the source; hence more studies need to be conducted on the size distribution, physical properties, and chemical characteristics of the heavy metal-laden particulates. The annual average deposition rates of particulate zinc, copper, and cadmium have been found to be in the decreasing order of 0.53, 0.18, and 0.064 g/m^2 per month, respectively, following the particulate lead.

The deposition rate of particulate lead, zinc, copper, and cadmium decreases with increasing distance from the stack. At this time, information on the radial distribution of metallic particulates settling upon the ground is not known, but will be obtained to estimate the heavy metal accumulation patterns.

Further studies are being conducted to determine the heavy metal concentration in airborne suspended particulates and to develop a model for the short and long-range atmospheric transport of metallic particulates discharged from the lead smelting operations.

COOPERATION AND SOCIETAL RELEVANCE

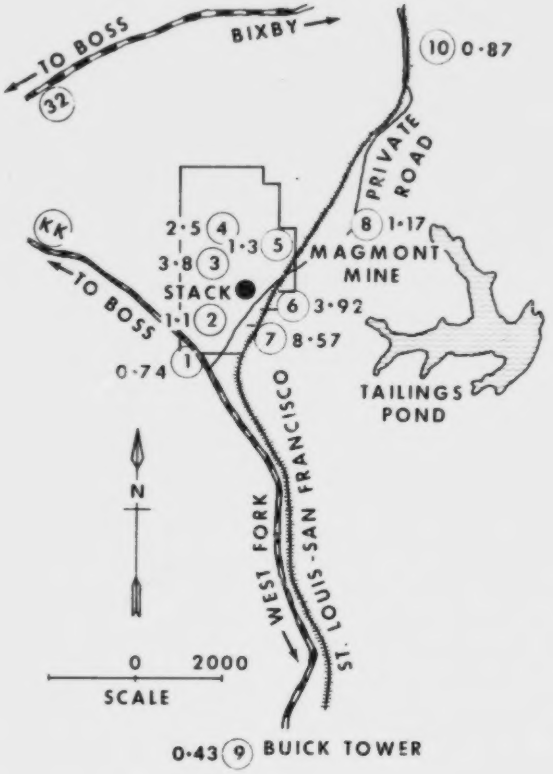

Figure 7. Settleable particulate lead–annual average (g/m^2–mo).

This research was initiated when industry and the public began to wonder if an industry could operate in a sensitive ecosystem without damaging a national park. The study has received the complete cooperation of concerned industries, the general public, and every local, Federal and State agency interested in the problem. Research findings have been applied by industries to control specific problem areas uncovered during this study. This unique cooperation has become a model for environmental cooperation and has been observed and cited as being of benefit to the local community and its surrounding (15).

The value of this cooperation was recently emphasized (16). This spirit of working together must be continued if needed mineral resources are to be developed without damage to the surrounding environment.

ACKNOWLEDGMENTS

The authors would like to acknowledge that this project was supported by the RANN (Research Applied to National Needs) Lead Study Program of the National Science Foundation. The AMAX Lead Company of Missouri and the St. Joe Mineral Corporation are due thanks for their continued support of research, technical assistance, and help. Sincere appreciation is also due to the Clark National Forest, the Missouri Clean Water Commission, the Missouri Air Conservation Commission, the Missouri Department of Conservation, the U. S. Bureau of Mines, and representatives from Region VII, EPA, Kansas City, Missouri, for their assistance and cooperation in this study.

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SOURCES OF TRACE METALS FROM HIGHLY-URBANIZED SOUTHERN CALIFORNIA TO THE ADJACENT MARINE ECOSYSTEM

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INTRODUCTION

The southern California coastal basin sustains one of the most rapidly growing urban complexes in the United States. Stretching more than 400 kilometers from Point Conception to the U.S.–Mexico border over an area of about 30,000 sq km (Figure 1), this basin is occupied by approximately 11,000,000 persons, or about five percent of the nation's population. Most of its population growth has occurred in Los Angeles and Orange Counties, in a pattern that now is being repeated in Ventura County to the north and San Diego county to the south.

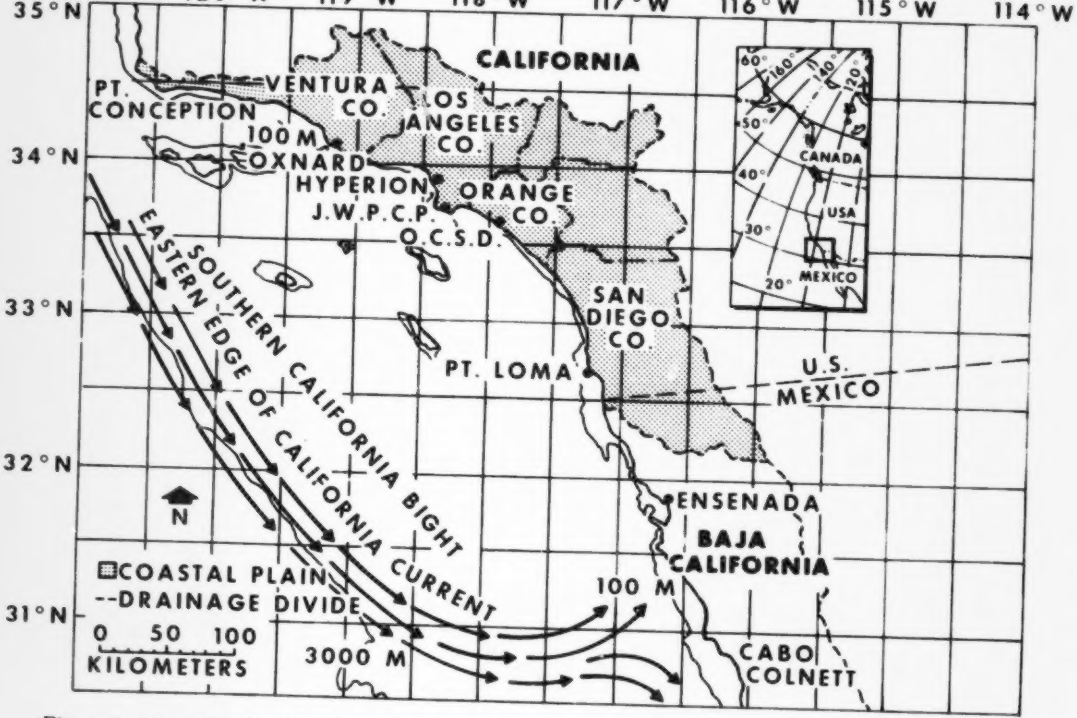
121°W
120°W
119°W
118°W
117°W
116°W
115°W
114°W
35°N
34°N
33°N
32°N
31°N
CALIFORNIA
PT. CONCEPTION
VENTURA CO.
LOS ANGELES CO.
100 M
OXNARD
HYPERION
J.W.P.C.P.
ORANGE CO.
O.C.S.D.
SAN DIEGO CO.
PT. LOMA
U.S.
MEXICO
SOUTHERN CALIFORNIA BIGHT
EASTERN EDGE OF CALIFORNIA CURRENT
N
ENSENADA
BAJA CALIFORNIA
100 M
3000 M
CABO COLNETT
COASTAL PLAIN
--DRAINAGE DIVIDE
0 50 100
KILOMETERS
60°
160°
140°
120°
50°
40°
30°
20°
CANADA
USA
MEXICO

Figure 1. The coastal plain of southern California and the adjacent marine waters of the Southern California Bight.

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The bordering Southern California Bight is bounded on the west by the California current. This current moves southward along the California coast past Point Conception, and turns landward several hundred kilometers to the south, impinging upon the coast in the vicinity of Cabo Colnett, Baja California, Mexico and forming the southern boundary of the Bight. Part of the current then turns north, joining a complicated circulatory pattern of the waters off southern California, while the remaining flow continues south (1).

The increasing urban, suburban, and industrial development has resulted in significant pollution problems in the coastal basin. Thus, the local municipalities and industries have turned to the Southern California Bight for disposal of liquid, and some solid, waste materials. The high mountain ranges, that run parallel to the coastline approximately 100 km inland, effectively trap air pollutants generated within the coastal basin, and facilitate transport of aerial contaminants, by fallout and rainout, and terrestrial contaminants, by surface runoff, to the Bight.

The adjacent marine ecosystem of the Bight is a major recipient of the wastes produced in the highly urbanized coastal basin. In this paper we will discuss the present state of knowledge of the trace metal inputs to the Bight. We will describe the nature of the various trace metal sources, estimate the magnitudes of potential sources and compare the significance of the inputs. The sources to be discussed include municipal wastewater discharges, discrete industrial and thermal discharges, surface runoff, vessel protective measures, ocean dumping, aerial inputs, and California current advective transport.

Figure 2 shows the locations of marine outfalls for municipal wastewaters (W), discrete industrial discharges (I), and cooling waters from power plants (P) in the Southern California Bight. Figure 2 also shows the major surface drainage channels along the southern California coast. Of these discrete sources, municipal wastewaters have received the most attention in the past.

MUNICIPAL WASTEWATERS

At present approximately 1,000,000,000 gallons (1000 mgd) of treated municipal wastewaters are discharged daily through marine outfalls to the Southern California Bight. Most of this, 84 percent, receives primary treatment only. Three major municipal wastewater discharges to the Bight occur within about 30 km of Palos Verdes Peninsula (Figures 1 and 2). Located off this peninsula is the Joint Water Pollution

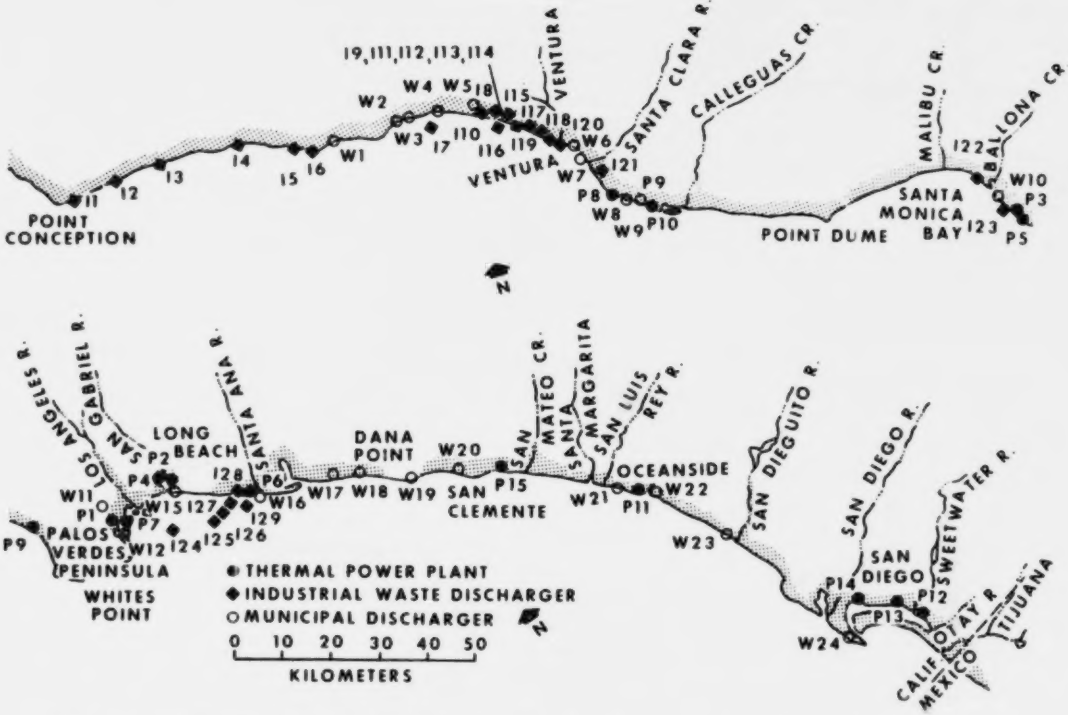
I9, I11, I12, I13, I14
VENTURA R.
SANTA CLARA R.
CALLEGUAS CR.
MALIBU CR.
BALLONA CR.
W2
W4
W5
I8
I15
I17
I18
I20
W6
W1
W3
I7
I10
I16
I19
VENTURA
W7
I21
P9
P8
W8
W9
P10
I1
I2
I3
I4
I5
I6
POINT CONCEPTION
POINT DUME
SANTA MONICA BAY
I22
W10
P3
I23
P5
N
LOS ANGELES R.
SAN GABRIEL R.
SANTA ANA R.
LONG BEACH
P2
P4
I28
P6
W11
P1
W15
I27
W16
I29
P7
P9
PALOS VERDES PENINSULA
W12
I24
I25
I26
WHITES POINT
DANA POINT
W17
W18
W19
W20
SAN CLEMENTE
P15
SAN MATEO CR.
SANTA MARGARITA
SAN LUIS REY R.
OCEANSIDE
W21
P11
W22
W23
SAN DIEGUITO R.
SAN DIEGO R.
SWEETWATER R.
SAN DIEGO
P14
P12
P13
W24
OTAY R.
TIJUANA
CALIF
MEXICO
● THERMAL POWER PLANT
◆ INDUSTRIAL WASTE DISCHARGER
○ MUNICIPAL DISCHARGER
N
0 10 20 30 40 50
KILOMETERS

Figure 2. Locations of discrete discharges (municipal wastewater, industrial and thermal discharges, and surface runoff) to the Southern California Bight.

Control Plant (JWPCP) outfall system (average length: 1.5 miles) of Los Angeles County Sanitation Districts, the largest of the municipal wastewater discharges in the Bight (370 mgd). To the northwest in Santa Monica Bay lie the 5 mile effluent and 7 mile digested sludge outfalls (335 and 5 mgd, respectively) of the Hyperion Sewage Treatment Plant of the City of Los Angeles; to the southeast lie the old 1 mile and new 5 mile outfalls of Orange County Sanitation Districts (130 mgd). The City of San Diego (90 mgd) discharges through the Point Loma outfall (2 miles); the City of Oxnard (12 mgd) discharges approximately one mile off the Ventura County coast. Altogether these five major dischargers contribute approximately 95 percent of the municipal wastewaters discharged into the Southern California Bight. These discharges occur at depths of 50 to 100 meters, generally below the thermocline.

Trace metal monitoring programs by the major dischargers were established prior to, or during, 1971. This has enabled us to complete a reliable estimate of trace metal mass emission rates from municipal wastewater discharges to the Bight for 1971. Table 1 shows the 1971 average concentrations of ten trace metals: silver, cadmium, chromium, copper, mercury, nickel, lead, zinc, iron, and manganese as reported by the major discharges.* It is to be noted that a variety of collecting, compositing, and analytical procedures were employed in the dischargers' routine monitoring programs. Figure 3 shows, as an example, the monthly variation of zinc concentrations in wastewater discharge. These time variations are typical of those for the other metals studied, and illustrate that, while individual monthly values can vary from the year-long mean by a factor of two or occassionally three, order-of-magnitude deviations are uncommon.

In order to evaluate the intercomparability of these concentration values reported by the various laboratories, we conducted a short term trace metal survey in the summer of 1971. With the assistance of plant personnel, week-long composite samples at each of the five major treatment plants were collected. Grab samples were collected by the regular procedures at one or two hour intervals for seven consecutive days. Every day these samples were filtered by 0.45-micron filters, and the residues and filtrates were frozen along with the unfiltered replicates. At the end of the collection period the water samples were thawed and combined into weekly composites which were immediately refrozen. The filtrate composites and daily residues were analyzed by atomic absorption spectrometry at the University of California, San Diego.† Unfiltered composites were submitted to the treatment plant laboratories for trace metal determination.

The results of this survey indicated generally good agreement between those metal concentrations reported by the treatment plant laboratories and the University of

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*The 1971 average concentrations of total suspended solids (mg/l) in the final effluents of these wastewater dischargers are: Oxnard – 80; Hyperion effluent – 73; Hyperion sludge – 3,000; JWPCP – 330; Terminal Island – 120; O.C.S.D. – 145; Pt. Loma – 110.

†This study was conducted in collaboration with J. Galloway, University of California, San Diego.

TABLE 1 AVERAGE CONCENTRATIONS OF TRACE METALS (mg/ℓ) IN FINAL EFFLUENTS OF MUNICIPAL WASTEWATER DISCHARGERS, 1971

Discharger	mgd		Silver	Cadmium	Cobalt*	Chromium	Copper	Mercury	Nickel	Lead	Zinc	Iron	Manganese	Remarks (note exceptions in footnotes)
W9 Oxnard	12													
		x	< .01	0.02		0.06	0.09	< .001	0.06	< .06	0.28	0.50	0.12	Avg. of Jan '71 & Mar '72 values
		s_x	–	0.00		0.02	0.01		0.01	–	0.08	0.18	0.01	
W10 Hyperion Effluent	335													
		x	0.002†	0.05	0.006	0.29	0.23	0.003	0.28	0.06	0.46	0.73	0.01†	Avg. of 12 monthly values
		s_x	0.001	0.02	0.002	0.07	0.03	0.001	0.04	0.02	0.07	0.09	0.01	
Sludge	5													
		x	0.03 †	0.23	0.03	2.1	12	0.10	2.6	0.51	16	47	1.6	Avg. of 12 monthly values
		s_x	0.003	0.05	0.005	1.3	1.6	0.01	0.33	0.15	2.1	8.8	0.78	
W11 JWPCP	371													
		x	0.02	0.03		0.86	0.56	0.001	0.24	0.25‡	2.4	9.9	0.13	Avg. of 12 monthly values
		s_x	0.03	0.002		0.03	0.03	0.0001	0.01	0.04	0.11	0.63	0.01	
W12 Terminal	8													
Island		x	0.002ƒ	0.01	< .006	0.11	0.26	0.001	0.42	0.00	0.36	0.94	0.05	Avg. of Jan. & July values
		s_x	0.00	0.01	.006	0.01	0.12	0.001	0.16	0.00	0.14	0.04	0.05	
W16 Orange	130													
Co. San. Dist.		x	0.02	0.06		0.22	0.35	0.001 #	0.16	0.22	0.54	1.2	0.09	Avg. of Oct. – Dec. values
		s_x	0.01	0.01		0.06	0.003		0.03	0.06	0.12	0.33	0.03	
W24 Pt. Loma	90													
		x		0.02		0.15	0.16	< .001	0.06	0.10	0.18			Avg. of July – Sept. values
		s_x		0.01		0.04	0.03		0.01	0.01	0.02			

*All cobalt concentrations are averages of 24-hr composite samples collected 24 Aug. and 9 Sept. 70.

†Hyperion effluent and sludge silver concentrations are averages of 4 monthly values; effluent manganese concentration is average of 11 monthly values.

‡JWPCP lead concentration is average of 10 monthly values.

ƒTerminal Island silver concentration is average of Aug. and Sept. 71 values.

#Orange Co. mercury concentration is estimated from analysis of 22 grab samples, 15 – 21 Jun 72.

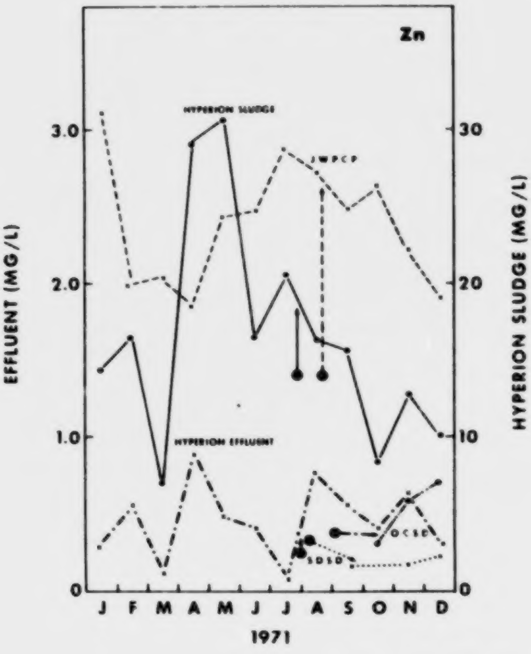

Figure 3. Concentrations of zinc observed during 1971 in municipal wastewaters of the major treatment plants along the southern California coast. Solid circles indicate concentrations measured in one-week composites of these wastewaters (2).

California, San Diego (2). The ratios of the two reported values usually were within a factor of two, and no trends were apparent. For those concentrations not reported by the treatment plants, comparisons between Galloway's data and the regular monitoring data for the closest collection period usually still showed a ratio of three or less. Figure 3 illustrates such comparisons for zinc.

Table 2 presents the percentages of trace metals that were found to be associated with the residue portions of the effluent samples. Although particles of smaller than 0.45-microns may be retained by the filter, the results do indicate a high degree of association between most of the metals and the wastewater solids. For silver, cadmium, chromium, copper, lead, zinc, and iron, 84 to 94 percent of the metals were associated with the residue. For cobalt, nickel, and manganese, these values range from 42 to 54 percent.

Although the data listed in Table 1 indicate considerable differences in average metal concentrations between the various wastewaters, the concentrations found on the wastewater particulates agreed much more closely, as is seen in Table 3. For example, the average 1971 metal concentrations (mg/l) in Hyperion effluent were generally 5 to 50 times lower than those in the digested sludge; however, on a particulate basis (mg/dry kg), the effluent concentrations in the composited effluent residue were generally only two to three times lower than those in the sludge residue. It is apparent that particulates play an important role in the wastewater transport of trace metals.

TABLE 2 PERCENT OF TRACE METAL RETAINED BY 0.45-MICRON FILTERS IN ONE-WEEK COMPOSITES OF FINAL EFFLUENT FROM MUNICIPAL WASTEWATER DISCHARGERS, SUMMER, 1971 (After Reference 2)

Discharger (data sampled)	Silver	Cadmium	Cobalt	Chromium	Copper	Nickel	Lead	Zinc	Iron	Manganese
W9 Oxnard (8/15-8/21)	87	92	50	90	91	80	92	94	90	40
W10 Hyperion Effluent (7/26–8/1)	75	88	50	64	86	35	90	86	80	34
W11 JWPCP* (8/13–8/19)	95	95	72	95	96	45	97	91	91	60
W16 Orange County (8/27–9/2)	97	98	–	81	94	57	97	94	93	44
W24 Point Loma (8/1–8/7)	85	91	42	90	90	74	92	94	91	30
$\bar{x}$	88	93	54	84	91	58	94	92	89	42

*The average of 23 weekly composite values for 1971 from monitoring data of Los Angeles County Sanitation District indicates that approximately 90% of the total mercury in JWPCP final effluent was retained on a 0.8-micron filter.

TABLE 3 TRACE METAL CONCENTRATIONS (mg/dry kg) IN WASTEWATER PARTICULATES* AND NATURAL MARINE SEDIMENTS OFF SOUTHERN CALIFORNIA (After Reference 2)

	Silver	Cad-mium	Cobalt	Chro-mium	Copper	Nickel	Lead	Zinc	Iron	Manga-nese
W9 Oxnard	30	115	15	350	1000	145	300	1500	9000	140
W10 Hyperion										
Effluent	130	108	4	1440	1500	520	320	2300	5400	108
Sludge	265	180	23	3430	2500	670	1000	4820	13000	156
W11 JWPCP	32	65	8	1700	1120	220	570	4100	20000	150
W16 Orange County	40	245	–	1330	1850	220	920	2330	7000	120
W24 Point Loma	105	65	8	1000	1600	310	545	3000	10000	200
Natural Nearshore Marine Sediment	1.0	0.4	7.2	46	16	14	8.5	63	25000	320

*Residue after filtration through 0.45-micron Millipore filter.

Table 4 presents the estimated annual trace metal mass emission rates from municipal wastewater discharges to the Southern California Bight.* This estimate indicates that approximately 95 percent of the trace metals carried by municipal wastewaters into the Southern California Bight are discharged from a coastline approximately 70 km in length. From a broad-scale point of view, the trace metal inputs from municipal wastewater to the Bight may be considered as a semi-point source centered around the Palos Verdes Peninsula.

DISCRETE INDUSTRIAL DISCHARGES

In contrast to the case for municipal wastewaters, where a few major discharges contribute most of the waste input, the situation for discrete industrial discharges is much more complex. The types of industrial processes and reclamation steps, if any, employed can play a vital role in the total quantity of a particular trace metal that is released in the discharge, irregardless of the volumetric flow rates. The first step in evaluating the importance of this source of trace metals to the Bight was to categorize the discharges in terms of the type of waste generated, the flow rate, and the location of the discharge. These data were obtained from the files of the local Regional Water Quality Control Boards, the state regulatory agencies for waste discharge into the waters of southern California.

Tabulations of such data for thermal cooling water and petroleum-related discharges along the coast are presented in Tables 5 and 6. No significant data on the concentration of trace metals in these discharges were located during the inventory compilation.†

One of the highly industrialized regions of the coast is the San Pedro Bay area. This is the site of Los Angeles-Long Beach Harbor, and is located just to the southeast of Palos Verdes Peninsula. In addition to the

TABLE 4 TRACE METALS MASS EMISSION RATES (M tons/yr) FROM MUNICIPAL WASTEWATER DISCHARGERS TO THE SOUTHERN CALIFORNIA BIGHT, 1971

Discharger	Flow (mgd)	Silver	Cad-mium	Cobalt	Chro-mium	Copper	Mer-cury	Nickel	Lead	Zinc	Iron	Manga-nese
W9 Oxnard	12	–	0.3	–	1	1	–	1	–	4	8	2
W10 Hyperion												
Effluent	335	0.9	23	2.8	130	110	1.4	130	28	210	340	5
Sludge	5	0.2	2	0.2	10	80	0.7	18	4	110	320	11
W11 JWPCP	371	10	15	–	440	290	0.5	120	130	1220	5100	67
W12 Terminal Island	8	–	0.1	–	1	3	–	5	–	4	11	1
W16 Orange Co.	130	3.6	11	–	40	63	0.2	29	40	97	220	16
W24 Point Loma	90	–	2.5	–	19	20	0.1	8	12	22	–	–
TOTAL	950	15	54	3.0	640	570	2.9	310	210	1700	6000	100

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*The corresponding input rate for total suspended solids is estimated to be 278,000 M tons/yr.

†An extensive analysis of the nature of thermal discharges to the Bight already has been presented elsewhere (3).

TABLE 5 ANNUAL DISCHARGE OF COOLING WATER FROM THE MAJOR POWER GENERATING STATIONS ON THE SOUTHERN CALIFORNIA COAST

	Generating station	Flow (10^8 cu m/yr)
FOSSIL-FUEL		
L. A. Dept. of Water and Power		
P1	Harbor – Wilmington	1.1
P2	Haynes – Seal Beach	10.5
P3	Scattergood – Playa del Rey	2.5
	Subtotal	14.1
Southern California Edison Co.		
P4	Alamitos – Seal Beach	11.6
P5	El Segundo – El Segundo	5.0
P6	Huntington – Huntington Beach	6.5
P7	Long Beach – Long Beach	0.8
P8	Mandalay – Oxnard	3.2
P9	Redondo – Redondo Beach	9.8
P10	Ormond – Ormond Beach	10.2
	Subtotal	47.1
San Diego Gas and Electric Co.		
P11	Encino – Carlsbad	2.2
P12	Silver Gate – San Diego Bay	2.2
P13	South Bay – San Diego Bay	5.0
P14	Station "B" – San Diego Bay	0.9
	Subtotal	10.3
NUCLEAR		
P15	San Onofre – San Clemente	5.5
	TOTAL	77.0

extensive recreational, commercial and naval vessel activities there, San Pedro Bay receives more than 150 discrete industrial waste discharges, either directly into the bay or via storm drains (see Table 7). The combined flow rate of these discharges, excluding cooling waters from power plants, is about 100 mgd, or about 10 percent that of the combined municipal wastewater discharges to the Bight. Approximately 10,000 metric tons per year of suspended solids are carried into the bay; this is about 3 percent of the total figure for the combined municipal wastewaters. As for the coastal industrial discharges, no significant data on trace metal concentrations in industrial discharges to the bay were located. As is seen in the table, the combined flow rate for metallic industrial discharge (3.8 mgd) constitutes only about 4 percent of the total industrial discharge to the bay. However, the significance of this low percentage should not be over emphasized. The lack of any significant trace metal data in the public files for the industrial discharges described above represents a serious gap in the knowledge of trace metal inputs to the Southern California Bight.

SURFACE RUNOFF

There are 200 to 300 surface runoff discharge locations along the southern California coast. However, approximately 70 percent of the average annual flow is carried by 15 major streams during the storm runoff season. The normal annual precipitation in the southern California coastal basin averages approximately 40 cm (15 in.), and surface runoff from about 60 percent of the drainage area is regulated by dams and other flood control measures. The southern California coastal streams generally carry appreciable flow only during and shortly following the occasional rainstorms.

In an attempt to characterize the surface runoff in the southern California basin, five major watersheds were selected for study during the storm season of 1971 to 72. These were the Santa Clara River, Ballona Creek, the Los Angeles, Santa Ana, and San Luis Rey Rivers (Figure 2).

In light of the apparent association of trace constituents with particulates, a survey was made on the relationship between flow rate and concentration of suspended sediment in southern California storm runoff.

TABLE 6 DISCRETE INDUSTRIAL WASTE DISCHARGERS OF THE SOUTHERN CALIFORNIA COAST

	Discharger	Type of waste	Flow (mgd)
I1	Phillips Petroleum – Point Conception	Oil brine Tanker ballast	0.2
I2	Texaco, Inc. – San Augustin	Oil brine	0.2
I3	Getty Oil – Gaviota	Oil brine Tanker ballast	0.16
I4	Shell Oil – El Capitan	Oil brine Tanker ballast	0.2
I5	Signal Oil & Gas – Ellwood	Oil brine Tanker ballast	0.29
I6	Atlantic Richfield – Coal Oil Point	Oil brine	0.06
I7	Standard Oil – Summerland	Oil brine	0.4
I8	Standard Oil – Carpinteria	Oil brine Tanker ballast	0.4
I9	Atlantic Richfield – Rincon	Oil brine	0.01
I10	Atlantic Richfield – Rincon Island	Oil brine	0.04
I11	Western Oil & Dev. – Rincon	Oil brine	0.36
I12	Petrol Industries – Rincon	Oil brine	0.01
I13	Continental Oil – Rincon	Oil brine	0.49
I14	Norris Oil Co. – Rincon	Oil brine	0.05
I15	Phillips Petroleum – La Conchita	Oil brine	0.36
I16	Phillips Petroleum – Punta Garda	Oil brine	0.4
I17	Mobil Oil – Sea Cliff	Oil brine Tanker ballast	0.18
I18	Continental Oil – Pitas Point	Oil brine	0.27
I19	Continental Oil – Grubb Lease	Oil brine	0.75
I20	Getty Oil – Ventura	Oil brine Tanker ballast	0.06
I21	Standard Oil – McGrath Beach	Oil brine	0.14
I22	McDonnell Douglas Corp. – Venice	Cooling tower bleedoff	0.65
I23	Standard Oil – El Segundo	Cooling water Refinery wastes	72
I24	Standard Oil – Island Esther	Oil brine	1
I25	Union Oil – Platform Eva	Oil brine	0.02
I26	Signal Oil and Gas – Platform Emmy	Oil brine	0.08
I27	Signal Oil and Gas – Huntington Beach	Oil brine	0.6
I28	Standard Oil – Huntington Beach	Oil brine	0.8
I29	Gulf Oil – Huntington Beach	Oil line ballast	0.01

TABLE 7 COMBINED FLOW RATES (mgd) OF DISCRETE INDUSTRIAL WASTE DISCHARGERS IN THE SAN PEDRO BAY AREA

Discharge area	Oil field brine	Oil line and tanker ballast	Refinery & petro-chemical	Metallic	Fish cannery	Miscel-laneous chemical	Total
L. A. Harbor	0.43	0.82	28	2.0	9.6	5.6	47
Long Beach Harbor	24	5.7	–	0.03	–	3.8	34
Dominguez Channel	0.05	–	6.5	1.4	–	2.3	10
L. A. River Tidal Prism	5.9	–	1.1	–	–	–	7
Los Cerritos Channel		–	–	0.12	–	0.04	0.2
San Gabriel River Tidal Prism	3.4	–	–	0.19	–	–	3.6
TOTAL	34	6.5	36	3.8	9.6	12	102

Data were provided by the United States Geological Survey from studies conducted during January and February, 1969. Typical examples of the relationship that was found for this abnormally wet year are illustrated for the Santa Clara River and the Santa Ana River in Figures 4 and 5, respectively.

It is seen that, over the four day periods, peaks in the concentration of suspended sediment clearly correlate with peaks in the flow rate. The peak amplitudes often are roughly proportional; this relationship, where applicable, has significant implications for programs aimed at the determination of mass emission rates of particulate-associated materials. For when the concentration (C_i) is proportional to the flow rate (F_i), e.g. $C_i = kF_i$, the transport rate (T) of the suspended substance increases as the square of the flow rate:

$$T = \sum_{i=1}^{n} C_i F_i = k \sum_{i=1}^{n} F_i^2 \qquad (1)$$

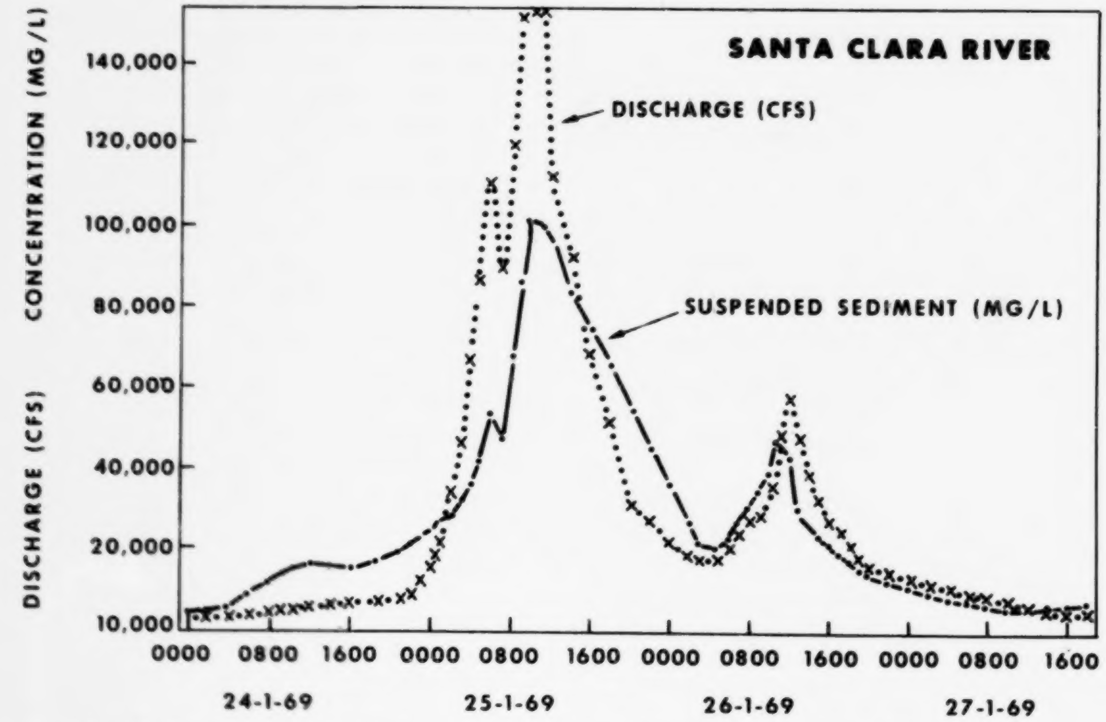

Figure 4. Comparison of discharge rate and suspended sediment concentration as a function of time in Santa Clara River storm runoff during January 24 to 27, 1969.

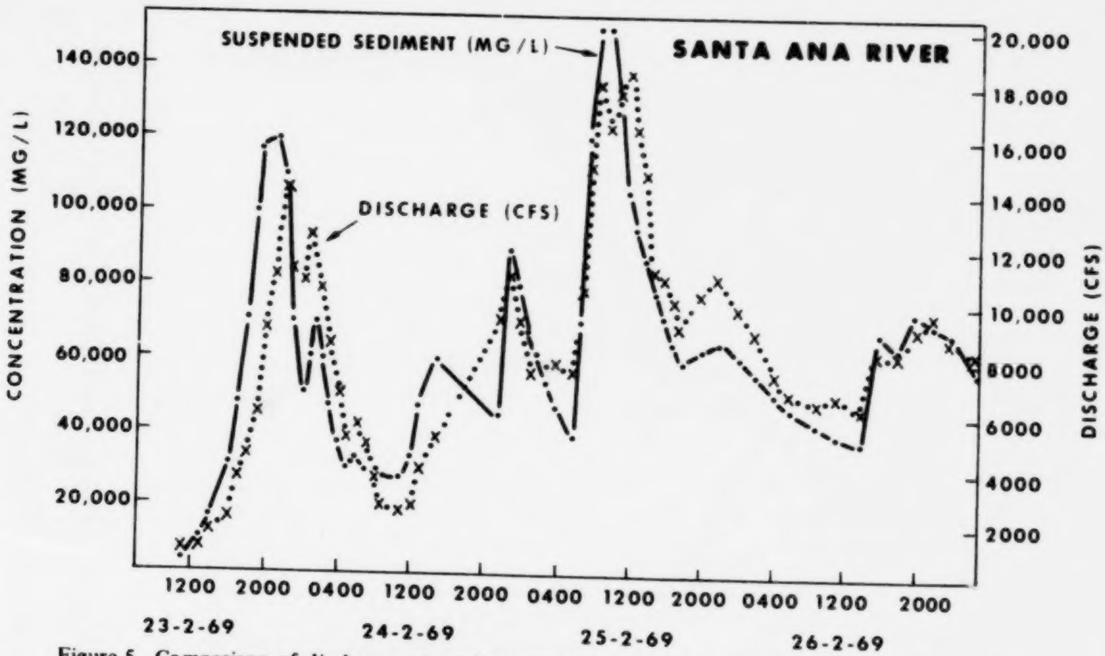

Figure 5. Comparison of discharge rate and suspended sediment concentration as a function of time in Santa Ana River storm runoff during February 23 to 26, 1969.

Under such conditions most of the transport of particulate-borne substances occurs during the period of peak flow. Sampling frequency therefore should be greater at these times to more accurately determine the total transport of the suspended material.

In order that representative samples of the storm runoff and its suspended sediments would be collected, a special depth-integrating sampler was constructed. This sampler was patterned after the United States Geological Survey suspended sediment pint sampler, but was enlarged to a one gallon capacity to provide sufficient sample for trace-level analyses. Other modifications also were made to decrease the chance of contamination; these will be reported in detail later. The collection stations were over the centers of the channels at bridges that were located as near to the coast as possible but above the tidal prism. As soon as possible after collection, generally within a few hours, the samples were taken to our laboratory where they were filtered through 0.45 micron filters. The filtrates and residues then were frozen until analyzed.

In this program, nine time series were obtained covering up to three storms in four channels. During periods of peak flow samples were collected at approximately two-hour intervals. The 1971 to 1972 period was an unusually dry year; all the channels did not flow at each storm, and no significant flow occurred in the San Luis Rey River and the southern streams during the year. Thus, the total surface runoff, estimated to be 242 x 10^6 cu m, including both storm and dry weather flow, was approximately 43 percent of the long term average for the Bight. Of the 167 x 10^6 cu m of storm flow to the Bight, during the year, approximately 60 percent was covered in this sampling program.

Analyses of these samples were conducted at the California Institute of Technology (4). Concentrations of ten trace metals, the same as for municipal wastewaters, were measured in the runoff filtrates and residues. Where necessary, concentration of the samples with ion exchange resin was employed, followed by measurement using atomic absorption spectroscopy. A detailed analysis of the data, including a comparison of individual metal inputs from the various basin types, is still underway, and, along with a description of analytical procedures will be reported later (4).

An example of the results for the total concentrations of silver, copper, and lead in storm runoff from Los Angeles River is presented in Figure 6, along with the flow rate and concentration of suspended sediment. These data illustrate the general correlation of peak values for flow rate, and silt and metal concentrations that was observed during this study. Calculations of mass emission rates for the ten metals studied were made from such concentration and flow rate data. Table 8 lists the estimates obtained to date for metal inputs to the Bight from runoff during water year 1971 to 72.* Also listed are the average values for percent of trace metal associated with particulates in the runoff samples. In

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*The corresponding input of suspended sediment (silt) to the Bight is estimated to be 274,000 M tons/yr.

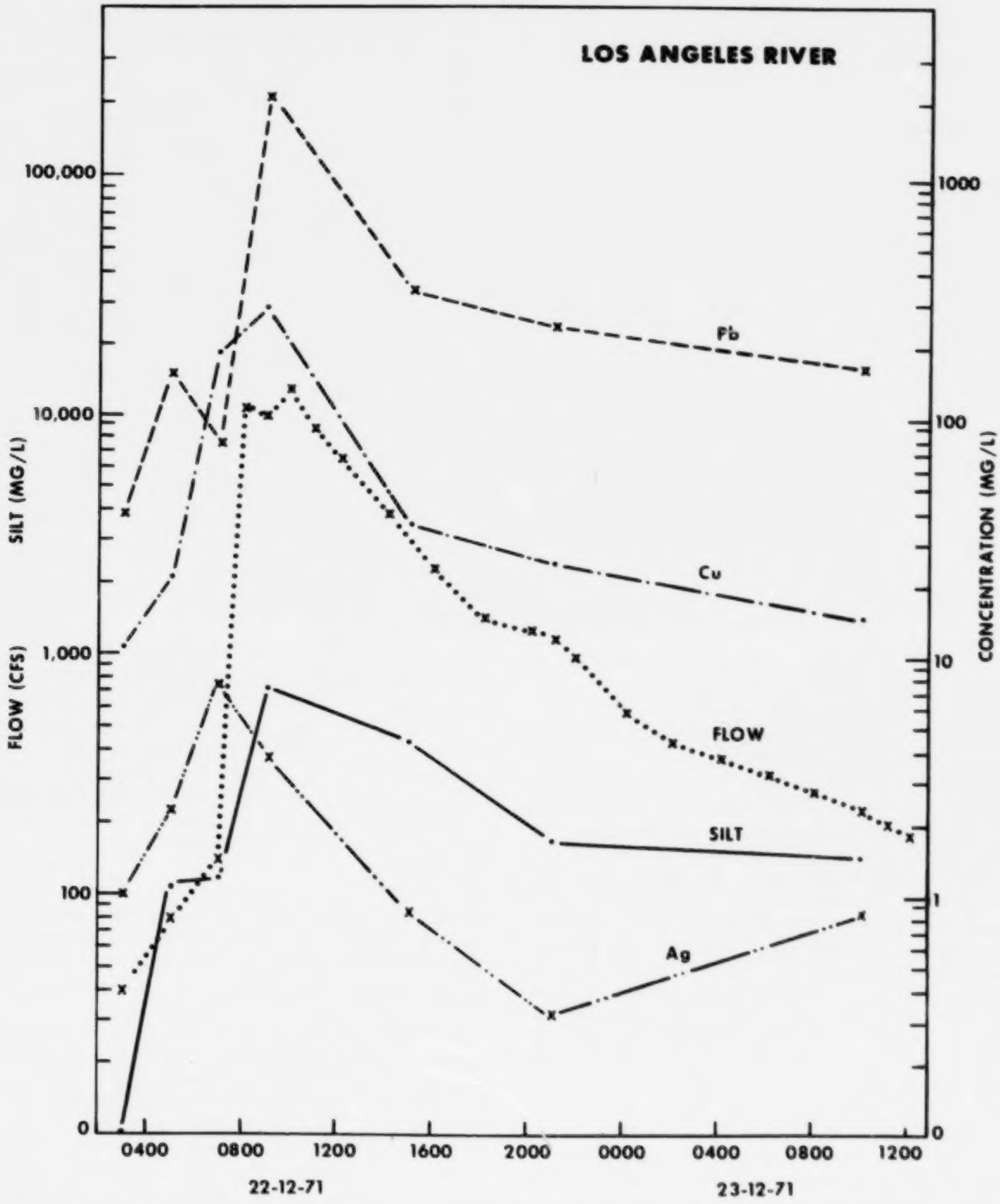

Figure 6. Concentrations of three trace metals and suspended sediment (silt) in the discharge (flow) of Los Angeles River during December 22 to 23, 1971.

general, these input rates were considerably lower than those for municipal wastewaters during 1971. For example, surface runoff inputs during the year constituted the following percentages of the 1972 municipal wastewater inputs of metals to the Bight: silver, 6.7 percent; cadmium, 1.9 percent; chromium, 3.8

TABLE 8 ESTIMATED TRACE METAL MASS EMISSION RATES (M tons/yr) FROM SURFACE RUNOFF TO THE SOUTHERN CALIFORNIA BIGHT, 1971–72

Metal	Mass emission rate	% particulate*
Silver	1.1	74
Cadmium	1.2	78
Cobalt	5.3	75
Chromium	25	82
Copper	18	59
Mercury	0.06	–
Nickel	17	63
Lead	90	89
Zinc	100	74
Iron	26000	99
Manganese	180	72

*Percent of metal retained by 0.45-micron filter.

percent; copper, 3.2 percent; mercury, 3.3 percent; nickel, 5.5 percent; zinc, 5.9 percent. Only for lead (43 percent), cobalt (170 percent), iron (430 percent), and manganese (180 percent) were the runoff inputs relatively important.

DIFFUSE SOURCES

In addition to the discrete or point sources of pollutants which have been discussed previously, there are a number of potentially significant pollutants whose sources to the Bight are distributed widely and thus are much more difficult to quantitate. Four such pollutant sources are vessel antifouling paint and fuel comsumption, ocean dumping, airborne inputs, and advective transport by the California current. Although these source categories have not been investigated thoroughly, preliminary analyses were conducted to provide a rough estimate of possible importance of these sources and to assist in establishing priorities for future studies. The following data on inputs from diffuse sources are order-of-magnitude estimates only and are presented here primarily to provide guidance for future studies.

VESSEL BODY PROTECTIVE MEASURES AND FUEL COMSUMPTION

The Southern California Bight harbors a large number of recreational, commercial, and naval vessels. Losses of bottom antifouling paint and anticorrosive anodes and spent fuel residues may represent important sources of trace pollutants to the marine environment.

To investigate the magnitude of these potential sources of pollutants, a preliminary survey of recreational vessel activity was undertaken. The two major objectives of this investigation were to inventory the recreational craft in each of the fourteen major marinas between Santa Barbara and San Diego, and to obtain preliminary information on the consumption, and presumed release to the Bight, of certain materials such as antifouling paint, sacrificial zinc anodes, and leaded fuel in one of the largest recreational vessel facilities, Marina del Rey in Los Angeles. Estimates of the quantities of trace metals used in bottom paints and in spent fuel in Marina del Rey could be extrapolated to estimate annual marina-related input of these metals to the Bight.

Antifouling Paints and Primers

The largest drydock in Marina del Rey, Windward Yacht and Repair, was studied to obtain an estimate of the use of antifouling paints. Of the 5,500 recreation craft in the marina, nearly 1,200 are hauled out and painted annually. Fifty to 60 gallons of antifouling paint are applied weekly; the old paint is removed and washed through a storm drain into the marina. Thus, this drydock uses approximately 2,860 gallons of antifouling paint annually, which corresponds to about 2.4 gallons per boat. Based on this analysis, it is estimated that approximately 13,000 gallons of antifouling paint are applied annually to the recreational craft moored in Marina del Rey. Assuming that vessel activity in the marina is typical of recreation craft in the marinas of the Bight, and extrapolating this unit paint consumption, it is estimated that the annual antifouling paint requirement for the 34,850 recreation craft in the Bight area is approximately 84,000 gallons. A gallon of antifouling paint weighs about 8.6 kg, which results in an estimated total annual paint usage rate of approximately 720,000 kg for recreational craft.

In a recent study conducted by San Diego Regional Water Quality Control Board (5) Barry estimated that the annual paint usage for commercial and naval vessels at the major shipbuilding and repair facilities in San Diego Bay was approximately 30,000 gallons of antifouling paint (8.6 kg/gal), 23,000 gallons of red lead primer (5.2 kg/gal), and 10,000 gallons of zinc chromate primer (4.1 kg/gal). It is estimated that, at the most, 10 percent of the paints or coatings removed by sand blasting of commercial and naval vessels is lost to the bay water. The bulk of the sand and coating residues is disposed of in land fills.

Comparable information for other major harbor facilities, such as the Los Angeles-Long Beach Harbor, is not yet available. If one assumes that San Diego Bay practices are representative of commercial and naval vessels generally, then the annual loss of antifouling paints and primers to the Bight is estimated to be as follows: Antifouling paint, 52,000 kg; red lead primer, 24,000 kg; zinc primer, 8,200 kg.

Estimation of the concentrations of trace constituents in antifouling paints and primers is difficult; however, the results from the Marina del Rey survey indicate that antifouling paints typically contain between 35 to 78

TABLE 9 ESTIMATED TRACE METAL COMPOSITION OF ANTIFOULING PAINT AND PRIMERS

Type	Trace metal	Average concentration (%)
Antifouling paint	Copper	50
	Mercury	0.5*
	Arsenic	0.2†
Zinc chromate primer	Zinc	45
	Chromium	12
Read lead primer	Lead	25

*Assuming that mercury content of mercury paints is 5% and that mercury paints comprise 10% of total paint usage.

†Assuming that arsenic content of arsenic paints is 2% and that arsenic paints comprise 10% of total paint usage.

percent cuprous oxide (31 to 69 percent as copper). Although the use of mercury compounds in marine paint was banned recently by the U. S. Environmental Protection Agency, some paints containing about 7 percent mercury phenate and 3 percent yellow oxide of mercury and unspecified concentrations of arsenic are still being sold.

Based on Barry's report, it is estimated that antifouling paints contain, by weight, up to 67 percent cuprous oxide, 3.4 percent mercury phenate, 1.3 percent mercury oxide, and 1.7 percent phenarsazine chloride (zinc compound). In addition, primers, apparently used mostly on the larger commercial and naval vessels, may contain up to 45 percent zinc, 12 percent chromium (as zinc chromate), and 25 percent lead (red lead primer).

From the limited information available, estimates have been made of the average trace metal concentrations of antifouling paints and primers (Table 9). Using the foregoing estimated concentrations of trace metals, the annual input of such materials from these sources has been estimated and are reported in Table 10.

Zinc Anodes

The use of sacrificial anodes to control galvanic corrosion provides another source of trace metals to the Bight. Investigations at Marina del Rey indicate that about 90 percent of the sail and power craft harbored there employ zinc anodes to control galvanic corrosion. It is estimated that each boat uses approximately 4 to 5 kg of zinc per year for this purpose. Thus, it is estimated that about 160 metric tons of zinc per year are contributed to the Bight from the use of zinc anodes, most of which go into the marina harborage areas.

Data furnished by Bunker Hill, Inc., a major supplier of anode material, indicate that zinc anodes also contain approximately 0.05 percent cadmium, implying that approximately 0.1 metric tons per year of cadmium enter the Bight from this source.

It should be noted that the foregoing estimates do not consider the sacrificial anode contribution from commercial and naval vessels because of the lack of specific information on this source. Hence the estimates appear to be quite conservative.

TABLE 10 ESTIMATED TRACE METAL MASS EMISSION RATES (M tons/yr) FROM RECREATIONAL, COMMERCIAL AND NAVAL VESSELS TO THE SOUTHERN CALIFORNIA BIGHT*

Source	Gross tonnage	Arsenic	Cadmium	Chromium	Copper	Mercury	Lead	Zinc
Recreational vessels								
Antifouling paint	720	1.4	–	–	360	3.6	–	–
Zinc anode	160	–	0.1	–	–	–	–	160
Fuel	–	–	–	–	–	–	3.5	–
Commercial and naval Vessels†								
Antifouling paint	52	0.1	–	–	26	0.3	–	–
Zinc chromate primer	8.2	–	–	1	–	–	–	4.1
Red lead primer	24	–	–	–	–	–	6	–
TOTAL		1.5	0.1	1	390	3.9	9.5	160

*Excludes ocean dumping contributions.

†No estimates for gross tonnage of zinc anodes and fuel used.

Leaded Fuel

Union Oil Company, which operates the only fuel dock at Marina del Rey, reports its annual fuel sales of about 440,000 gallons of low-lead gasoline (containing 0.5 gm Pb/gallon) and 110,000 gallons of high octane gasoline (containing 3 gm Pb/gallon). Thus, the consumption of these fuels results in the release of about 0.55 metric tons of lead per year to the Bight from Marina del Rey fueled craft. If these fuel consumption and lead release data are applied to all recreational craft moored in the Marinas of the Southern California Bight, an input of lead to the Bight of approximately 3.5 metric tons per year is obtained.

Trace Material Mass Emission Rates

Table 10 presents a summary of the annual mass emission rates for trace metals reaching the Bight from selected sources associated with recreational, commercial, and naval vessel activity. It is recognized that some of the estimated inputs are crude; however, they represent the best information available. Moreover, it should be noted that the estimated vessel related mercury input of 4 metric tons per year is greater than the total input of mercury from treated municipal wastewater and surface runoff. The estimated vessel related input of copper (390 M tons/yr) is about two-thirds of the corresponding copper input to the Bight from municipal wastewater runoff.

OCEAN DUMPING

In an investigation of past ocean dumping practices, data on eight major types of wastes dumped from vessels into the Bight was reviewed. These were: (a) refinery wastes, (b) chemical wastes, (c) filter cake, (d) oil drilling wastes, (e) refuse and garbage, (f) radioactive wastes, (g) military explosives, and (h) miscellaneous types of wastes.

Figure 7 shows the location within the Southern California Bight of both active and inactive ocean dumping sites. Fourteen ocean dumping sites, which were approved either by the U. S. Army Corps of Engineers or by the California Regional Water Quality Control Boards, have been designated for waste dumping purposes since 1931. At present, dumping of various types of wastes at nine designated sites is prohibited by regulatory agencies, and disposal of military explosives at two other sites is still under moratorium issued by the Department of Navy in 1971.

Table 11 lists the major dumping sites, the total tonnage dumped during various periods, and the estimated present annual dumping rate for each type of waste.

Refinery Wastes

It is estimated that approximately 480,000 metric tons of petroleum refining wastes were dumped between 1946 and 1971, corresponding to an annual average of

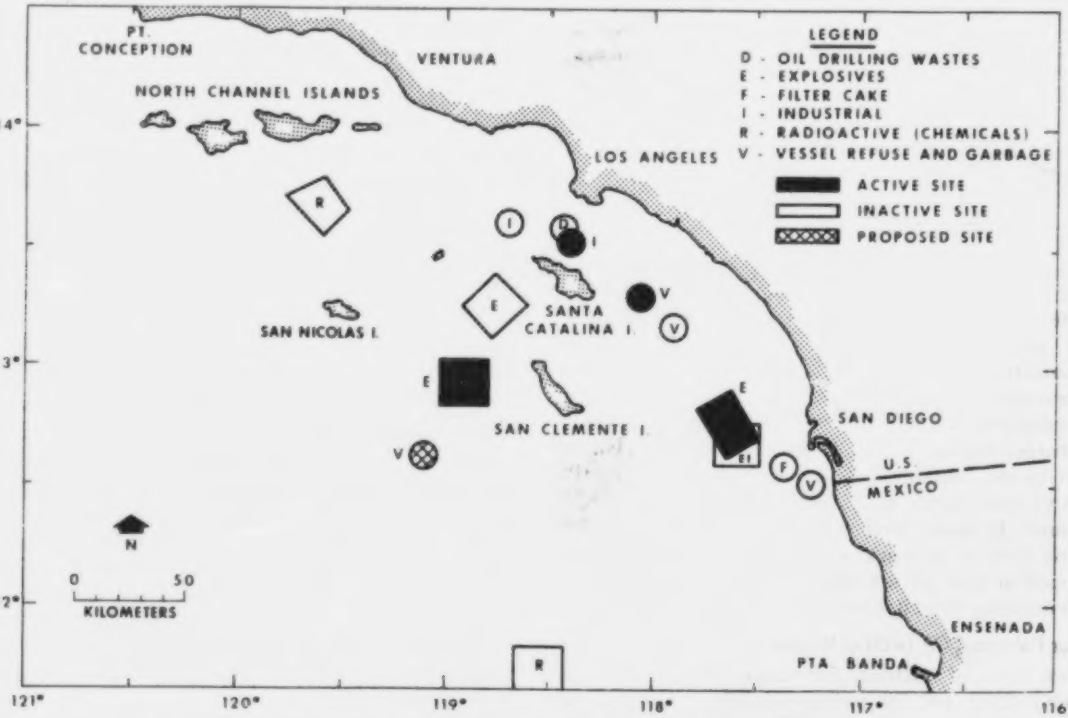
PT. CONCEPTION
VENTURA
NORTH CHANNEL ISLANDS
LOS ANGELES
LEGEND
D - OIL DRILLING WASTES
E - EXPLOSIVES
F - FILTER CAKE
I - INDUSTRIAL
R - RADIOACTIVE (CHEMICALS)
V - VESSEL REFUSE AND GARBAGE
ACTIVE SITE
INACTIVE SITE
PROPOSED SITE
R
I
D
I
E
V
SANTA CATALINA I.
V
SAN NICOLAS I.
E
E
SAN CLEMENTE I.
EI
F
V
V
SAN DIEGO
U.S.
MEXICO
N
0
50
KILOMETERS
ENSENADA
PTA BANDA
R
34°
33°
32°
121°
120°
119°
118°
117°
116°

Figure 7. Locations of ocean dumping sites in the Southern California Bight.

TABLE 11 SUMMARY OF WASTES DUMPED INTO THE SOUTHERN CALIFORNIA BIGHT, 1931–71

Type of waste	Record period	Estimated total during record period (M tons)	Estimated present tonnage* (M tons/yr)
Refinery wastes	1946–71	480,000	1,800
Chemical wastes	1965–71	2,800	470
	1947–71	5,700	210
	1960–67	140	–
Filter cake	1969–70	320,000	–
Oil drilling wastes	1966–70	3,000,000	–
Refuse and garbage	1931–71	47,000	1,200
	1944–70	7,400	–
	1947–68	90,000	–
Radioactive wastes	1946–68	–	–
Military explosives	1945–70	–	–
Miscellaneous wastes	–	–	250

*Wastes for which no present tonnage estimate is given have been discontinued (military explosives by moratorium).

about 18,000 metric tons per year. However, the reported annual dumping rate has dropped to about 1,800 tons per year since 1968. The principal dumping site for refinery waste is in the San Pedro Channel. The specific composition of these refinery wastes are unavailable; however, they are believed to include spent caustic solutions, acid sludges, spent catalysts, petrochemical wastes, and chemical cleaning wastes. These materials surely must include trace metals, trace organics, and other potentially toxic substances, but quantitative information is not available.

Chemical Wastes

This type of industrial waste is dumped either in sealed containers or in bulk by tank barge, and includes waste material from aerospace, heat-treating, plating, film processing, chemical processing, and electronic manufacturing firms, industrial, medical, and academic laboratories, and military and other sources. Most of the recorded bulk tonnage, 210 metric tons/yr since 1947, is discharged approximately 15 km east of Catalina Island. Most of the containerized chemical wastes, 470 metric tons/yr since 1965, have been dumped in San Pedro Channel. Between 1960 and 1967, approximately 140 metric tons of chemical waste, sodium cyanide, were dumped in bulk 32 km west of Point Loma. However, such dumping there has been prohibited since 1967.

Filter Cake and Oil Drilling Wastes

Two types of relatively inert material, filter cake, 70 percent fixed and 30 percent volatile solids, and oil drilling wastes, similar to dredging spoils, were dumped to the Bight in large amounts for a short period. Filter cake, consisting of about 50 percent perlite and 50 percent cellulose, is used in extraction of algin from kelp, and approximately 320,000 metric tons were dumped about 15 km west of Point Loma during 1969 and 1970. More than 3 million metric tons of oil drilling mud and cutting were dumped in the San Pedro Channel between 1966 and 1970. These two types of dumpings have been prohibited and discontinued since 1970.

Refuse and Garbage

Until recently, naval vessel refuse and garbage has been dumped into the Bight. Between 1947 and 1968, an estimated total of 90,000 metric tons were dumped in the vicinity of the Coronado Islands, and between 1944 and 1970 an estimated total of 7,400 metric tons were dumped 40 km southeast of Catalina Island. However, approximately 1,200 metric tons per year of refuse and garbage from commercial vessels is still being dumped approximately 16 km east of Catalina Island.

Other Types of Waste

Between 1945 and 1970, undetermined quantities of unspecified military explosives and toxic chemical ammunition have been dumped in several designated dumping sites in the Bight. Low-level radioactive wastes also have been dumped in the authorized locations during the period of 1946 to 1968. Dumping of military explosives and other wastes has been interrupted by a moratorium issued by the Navy in 1971. Dumping of radioactive wastes has been terminated since its prohibition in 1968.

Based on information furnished by H-10 Water Taxi Company, Los Angeles, approximately 250 metric tons per year of undefined miscellaneous wastes are dumped in the Southern California Bight.

Trace Constituent Mass Emission Rates

Although there has been an attempt to quantify the distribution and amount of wastes in selected types dumped into the Bight, virtually nothing has been found in the public record regarding the concentration of specific pollutants in the wastes dumped. Thus, for pollutants such as trace metals, estimation of mass emission rates from this source is very difficult. Nevertheless, order-of-magnitude estimates of the probable upper limits of such mass emission rates have been attempted. It appears that only refinery and chemical wastes and some undefined miscellaneous wastes currently constitute any significant source of trace pollutants to the Bight. As shown in Table 11, it is estimated that approximately 1,800 metric tons per year of refinery waste and 1,000 metric tons per year of chemical and miscellaneous wastes were dumped into the Bight off Los Angeles and San Diego in 1971. It seems reasonable to assume that, on the average, these wastes would not contain more than 0.5 to 1 percent, by weight, of any one of the trace constituents being investigated by Southern California Coastal Water Research Project, with the exception of iron and zinc. It is likely that these wastes might contain up to 2 percent zinc and 10 percent iron. Owing to the value of mercury and silver, upper limits for their average concentrations are assumed to be an order-of-magnitude lower than the general level taken for most of the other metals. Based on these extremely rough assumptions, upper limit estimates of present annual trace metal mass emission rates are presented in Table 12.

AERIAL FALLOUT

Limited data are available on aerial fallout rates of trace metals to the Bight. This source is difficult to quantitate for several reasons, including the high horizontal velocity compared to the vertical velocity of airborne particles, the diffuse nature of the source, the relatively high constituent gradients that may exist near the densely-populated areas, and the large area of the Bight.

Rainfall Washout

Several recent studies have provided some insight into this subject. Estimates of metal contributions from rain falling directly on the Bight (6), conducted on Catalina Island from September 1966 to January 1967, are shown in Table 13. The median metal concentration values were used, and an average annual rainfall rate of 40 cm (15 in) over a Bight area of 100,000 sq km was assumed. It should be noted that these data do not include the contribution of metals to the Bight from dry fallout.

The results of this rough estimate indicate, as seen in the summary Table 15, that the mass emission rate of lead from direct rainfall washout on the Bight is significantly higher than that from the discrete sources, municipal wastewater and surface runoff. The mass emission rates of nickel and iron from direct rainfall washout, on the contrary, are much lower than those from the discrete sources to the Bight. For copper,

TABLE 12 UPPER-LIMIT ESTIMATES OF TRACE METAL MASS EMISSION RATES TO THE SOUTHERN CALIFORNIA BIGHT FROM OCEAN DUMPING

Metal	Assumed maximum concentration (% by wt)	Est. max. mass emission rate* (M tons/yr)
Silver	0.05	1.5
Cadmium	0.5	14
Cobalt	0.5	14
Chromium	1	28
Copper	1	28
Mercury	0.05	1.5
Nickel	1	28
Lead	1	28
Zinc	2	56
Iron	10	280
Manganese	1	28

*Based on estimated 1971 dumping tonnage of 1800 M tons/yr of refinery wastes and 1000 M tons/yr of chemical and miscellaneous wastes.

TABLE 13 ESTIMATED TRACE METAL MASS EMISSION RATES FROM DIRECT RAINFALL ON THE SOUTHERN CALIFORNIA BIGHT

Metal	Median concentration* in rainwater (µg/ℓ)	Mass emission rate (M tons/yr)
Copper	10	400
Mercury	0.2	8
Nickel	1	40
Lead	25	1000
Zinc	55	2200
Iron	1	40
Manganese	12	480

*From Reference 6.

mercury, zinc, and manganese, comparable amounts are contributed from rainfall washout and discrete sources.

Dry Fallout

It is possible that the contribution of particulate-borne materials to the Bight via dry fallout may exceed those due to direct rainfall washout. For example, the fallout rate of lead on dust particles (24 mg Pb/m^2-yr) was about two to three times as large as that due to rainfall (10 mg Pb/m^2-yr) (7). Isotopic analysis confirmed that this lead was not of soil origin, but that essentially all of it originated in the combustion of leaded gasoline. Extrapolation of the La Jolla fallout rates to the entire Bight yields annual lead input rates through dry and wet fallout of approximately 2,400 and 1,000 metric tons, respectively. It is interesting to note that the latter value is about the same as that obtained by extrapolating the Catalina Island rainfall data (6).

In 1968, approximately 23,000 metric tons of lead were combusted in gasoline in California (7). It is probable that at least half of this comsumption occurred in southern California. Thus, approximately 10,000 metric tons of lead are released annually to the atmosphere in this area. The previous data suggest that as much as one-third of this amount may fall directly into the coastal waters, depending upon the degree to which fallout rates at La Jolla and Catalina Island are representative of fallout to the entire Bight.

ADVECTIVE TRANSPORT

At the regional scale considered here, a potentially significant but largely unevaluated source of trace metals transported into the Southern California Bight is the California current which carries seawater and associated constituents into the Bight (Figure 1). The complex flow pattern keeps the water in the Bight for some time, during which time various physical, chemical, and biological processes can occur. These processes may result in the retention of significant amounts of some constituents in the Bight. These processes may also result in the removal of significant amounts of other constituents from the Bight in the advective flow from the Bight.

Mass Emission Rates

The surface area of the Bight has been estimated to be about 1×10^{11} sq m. Assuming the mixed surface layer depth to be 50 m, the volume of the mixed layer of the Bight is computed to be 5×10^{12} cu m. It has been shown that the mean residence time of water in the mixed layer is on the order of 3 months (1). Thus the advective flow rate of the California current is estimated to be approximately 2×10^{13} cu m/yr.

Assuming that the trace metal concentrations reported for ocean waters are representative of California current waters, the mass transport rates of trace metals into the Bight by the California current are estimated to be as shown in Table 14. Although the role of the California

TABLE 14 ESTIMATED TRACE METAL MASS TRANSPORT RATES TO THE SOUTHERN CALIFORNIA BIGHT BY THE CALIFORNIA CURRENT

Metal	Concentration (µg/ℓ)	Mass transport rate (M tons/yr)
Silver	0.3	6,000
Cadmium	0.1	2,000
Cobalt	0.4	8,000
Chromium	0.2	4,000
Copper	3	60,000
Mercury	0.03	600
Nickel	7	140,000
Lead	0.3	6,000
Zinc	10	200,000
Iron	3	60,000
Manganese	2	40,000

current as a source of trace metals to the Bight may be different from those of other sources, the estimated mass transport rates of most of the trace metals by advective transport far outweigh the mass emission rates from other sources. For example, the mass transport rate of mercury by the California current is estimated to be about 600 metric tons per year, which is about 30 times the amount of mass emission rates of mercury from all other sources to the Bight (8). However, for chromium, lead, and iron, the annual advective transport rates exceed the sum of the other, principally terrestrial inputs by only a few factors. At least for chromium and lead, whose terrestrial inputs are believed to be largely anthropogenic, these inputs appear to be a significant perturbation to the natural mass balance of metals in the Bight.

The circulation of marine waters off southern and Baja California is such that increased levels of trace constituents in the biota to the west and south of the densely populated southern California coastline may in fact be due to sources far to the north. For example, anomalously high levels of zinc–65 were found in the coastal mussel, *Mytilus californianus*, collected during 1963 to 64 from northern Baja California, where the California current sweeps eastward and impinges on this coast (9). The suggestion that this anomalous zinc–65 was being carried by the California current was further supported by increasing concentration of this radiometal in samples of the oceanic gooseneck barnacle, *Lepas anatifera*, collected toward the west off southern California. In contrast to zinc–65, the other two radiometals measured, cobalt–60 and manganese–54, did not show significant differences between the nearshore of La Jolla and California current speciments. The levels of these two nuclides also were approximately constant in *M. californianus* from both the southern California and Baja California stations. This argues against nuclear fallout as the source of the anomalous zinc–65, and suggest that the Columbia River effluent, which carried approximately 55,000 pCi zinc–65 per month into the water off Washington and Oregon, was elevating zinc–65 concentrations in the marine biota 1,900 km to the south. Therefore, the dense population center off San Francisco, and the intense agricultural activity in the large central valley of California, both may be important source regions of runoff and airborne pollutants that are introduced into the California current north of Point Conception. Any such contaminants from the north could contribute to elevated levels in the marine biota to the west and south of southern California.

There is another important aspect of possible pollutant transport from the north. As the California current moves slowly down the coast of California, certain trace constituents introduced into the surface layer off Washington, Oregon, or northern California may be incorporated into the food web. If these substances are subject to trophic or feeding level concentration, higher levels might be expected in a specified organism caught off southern California, compared to levels observed in the same organism caught to the north. Ocean current advection from the north could play an important part in contributing to elevated levels of certain pollutants in the biota off southern and Baja California.

SUMMARY

In Table 15 we have summarized our estimates of trace metal annual mass emission rates to the Bight from the various sources for which sufficient data are available. Although the values are not all of comparable reliability, and several potentially important modes are not quantified at all, the summary does provide useful insight into which of the input modes studied are of

TABLE 15 ESTIMATED TRACE METAL MASS EMISSION RATES (M tons/yr) FROM VARIOUS SOURCES TO THE SOUTHERN CALIFORNIA BIGHT, 1971

Metal	1 Municipal wastewater	2 Surface runoff	3 Direct rainfall	4 Vessel* coating	5 Ocean dumping maxima	6 Sum of col. 1 through 5	7 Advective transport
Silver	15	1	–	–	2	18	6,000
Cadmium	54	1	–	0.1	14	69	2,000
Cobalt	3	5	–	–	14	22	8,000
Chromium	640	25	–	1	28	690	4,000
Copper	570	18	400	390	28	1,400	60,000
Mercury	3	0.1	8	4	2	17	600
Nickel	310	17	40	–	28	400	140,000
Lead	210	90	1,000	10	28	1,300	6,000
Zinc	1,700	100	2,200	160	56	4,200	200,000
Iron	6,000	26,000	40	–	280	32,000	60,000
Manganese	100	180	480	–	28	790	40,000

*Including vessel antifouling paints, primers, and spent fuel residues.

probable importance. For example, of the estimated input routes of locally derived copper and mercury, municipal wastewater discharge, vessel antifouling paint, and direct rainfall all appear to have about the same importance. For zinc, municipal wastewater and direct rainfall appear to predominate. In the case of lead, the surface runoff input is the same order as that of municipal wastewaters, but these sources probably contribute an order of magnitude less lead to the waters of the Bight than does aerial fallout. Cobalt, iron, and manganese are the only other trace metals studied that have surface runoff inputs of approximately the same importance as those of municipal wastewaters, and the inputs of these metals via both modes may be more dependent on natural than anthropogenic sources. However, for silver, cadmium, chromium, and nickel, present data suggest that municipal wastewater discharge to the Bight dominate all other locally-derived inputs. Clearly, more comprehensive and reliable information on the importance of wet and dry fallout, and of vessel-protective measures, are needed in the above comparison. Further, the lack of any reliable estimates of inputs of trace metals from direct industrial discharges represents a major deficiency in this mass balance attempt. Correction of these various deficiencies probably should assume a higher priority than improving our knowledge on the inputs from ocean dumping, as the present best estimates of probable maximum values suggest that only for cobalt does it appear likely that ocean dumping could represent the major local source. With the exception of chromium, lead, and iron, for each of the trace metals studied the sum, see column 6, Table 15, of all estimated yearly inputs eminating from the coastal plain of the Bight is one to two orders of magnitude below the estimated annual flux of the metal through the Bight via ocean current advection. Although this situation may be natural in the case of iron, the fact that local anthropogenic inputs of the other two metals are, to the first order comparable to that of gross advection suggests that chromium and lead transport from the urban areas may represent a specially important perturbation of the natual metals budget for the regional ecosystem. However, it is difficult to draw any very reliable conclusions from the comparison of local versus advective inputs until more is known about the net addition of metals to, or removal from, the Bight due to bottom sediment interactions and to ocean circulation. Further, the physical-chemical state of a metal advected into the Bight may be significantly different from that injected via a particular local input mode. In addition to better data on input rates of a particular trace metal to the Bight, much more needs to be learned about (a) the nature of the metal being transported to the local marine waters, (b) the changes that take place in the metal following introduction to these waters, and (c) the transport processes and eventual fate of the metal in the ocean ecosystem.

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OVERVIEW OF EFFECTS OF TRACE METALS

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We may look on the environmental effects of trace metals from the very narrow viewpoint of the immediate effects upon the human population or from the much broader viewpoint of their effects upon the various components of the total environment including man. It is important, I think, to take the broadest viewpoint, first because man can be indirectly affected by accumulations of pollutants in any part of his environment, and second because mankind should have a concern for other living species as well as for the future generations of his own species.

Trace metals may be classified as to those essential to life and those not known to be essential to life processes. Of those known to be essential for at least some species of life, we may list iron, copper, zinc, manganese, cobalt, nickel, molybdenum, and vanadium. Some metals, formerly thought to act only as poisons, are recognized to be micronutrients at very low concentrations. Among these are selenium, chromium, and arsenic (1). Even cadmium has been listed as a micronutrient, and some authorities have speculated that all elements for which organisms develop a tolerance might be essential for some function. Lead is an element for which there is no known beneficial function, but which is so wide-spread as to be detectable in all plants and animals.

A typical biological response curve would show an increasingly beneficial effect with increasing concentration up to a certain optimum level. Beyond this level, there is a tolerance region which may be either relatively narrow or broad, beyond which benefits decrease, injurious effects begin, and finally a lethal dose is reached. For those elements not known to be essential, the first region of the response curve is missing, but there is generally a tolerance region followed by the toxic and lethal dose regions. In this group of metals, we can list at least theoretically all metals not included among the major or minor essential elements. Of greatest concern, of course, are those known to be toxic at low or moderate concentrations, for example, cadmium, mercury, and lead.

Trace metals are introduced into the environment by several mechanisms. First of all, it is important to distinguish between natural and man-made distribution, because the former constitutes a background level against which man-made pollution can be measured. Among the natural mechanisms, we should include weathering and leaching of minerals, with distribution via natural waters or air borne particulates. Also, volcanic action and natural gases are known to introduce substantial quantities of certain metals, notably mercury, into the environment. Among the man-made sources we can recognize three important mechanisms. First, particulate matter enters the atmosphere from smoke stacks, incinerators, open fires, and automotive exhausts. The latter source accounts for the introduction of most of the lead. The second source is in the form of liquid solutions, either industrial wastes and effluents or municipal sewage. Trace metals entering sewage tend to be concentrated in sewage sludge, the disposal of which may spread the metal through the environment if the sludge is used for agricultural purposes or landfill. The third source of trace metals is through chemicals applied to the soil as pesticides. In a listing (2) of 280 pesticides, heavy metals were mentioned 141 times in 112 of the formulations. The listings mentioned mercury 45 times, copper 28, zinc 24, cadmium 13, manganese 12, chromium 7, tin 5, nickel 4, iron 3, and lead 1. In 1970, 90,000 tons of fungicides were used in agriculture in the United States. In that same year, 204,000 pounds of mercury-containing fungicides were used in the United States and one million in the world as a whole. Presumably this usage has been strongly curtailed since that time.

The main mechanisms of movement of trace metals are through air borne particulate matter and through the movement of natural waters. Rainfall and snowfall represent mechanisms whereby particulate matter is removed from the atmosphere and into surface waters either as dissolved or suspended matter or sediments. Heavy metals tend to be concentrated preferentially in the suspended matter of water rather than being in true solution, but both suspended matter and solution present mechanisms of transport. Of the trace metals in solution, electrochemical methods can distinguish between labile and bound metal. The distinction is that, of the total heavy metal contained in solution, only a portion responds to the electroanalytical method, for example anodic stripping voltammetry, if the natural water sample is analyzed as received. On the other hand, if the sample is acidified, then the electrochemical method shows the total heavy metal content of the sample. It is believed that the natural water sample contains complexing agents which tie up the metal ions, for example lead or copper ions, in a form to which the method does not respond. Acidification releases the metal ions from the bound into the labile form. Further evidence as to the nature of the binding is revealed by the technique of gel permeation chromatography (3). If the natural water sample is percolated through a gel permeation chromatography column, the various fractions indicate the presence of traces of organic matter of relatively high molecular weight, of the order of 10,000, presumably originating from sources such as humic acids.

Exactly what the significance of such binding of heavy metals in natural waters is, is not at all clear at the present time, from the viewpoint of uptake of metals by plant or animal life. It is possible, of course, for natural complexing agents to solubilize heavy metals from minerals. In the same way, there has been concern over the possibility that man-made complexing agents such as NTA may solubilize metals held in insoluble form. As far as I am aware, there is no evidence that NTA used as an additive in detergents could act in this way, because its biodegradability would prevent the buildup of appreciable concentrations.

Another form of binding of metals in natural waters is by adsorption on inorganic colloids, for example, clays. Both in natural waters and in soils, clays are known to bind heavy metals very tenaciously so that only a very small fraction of the metal content in waters or soils are present in true solution. We have found, for example, that a clay-rich soil heavily treated with additions of soluble lead salt shows less than 1 ppm of soluble lead in the soil moisture. Nevertheless, it turns out that a plant can extract heavy metal from the insoluble as well as the soluble components present in soil. This will be discussed in further detail later.

The biological effects of trace elements need a great deal more thorough investigation. First of all, it is simplistic to list elements as I have done without specifying chemical forms. The widely differing toxic effects of different forms of mercury are well known by now, but the same situation must pertain to most elements to greater or lesser extent. Thus chromium (VI) is much more toxic than chromium (III). Cobalt is an essential element to higher organisms in the form of vitamin B_{12} but useless and even toxic in inorganic forms. Inorganic cobalt is converted to vitamin B_{12} only by lower organisms, to which inorganic cobalt is essential at low concentrations.

As mentioned previously, plant roots can extract trace metals from forms that are insoluble in soil moisture. This can be demonstrated by a simple experiment. If a plant such as a corn plant is grown in a hydroponic culture, containing lead, the uptake by the leaves or stalks of the corn plant is roughly comparable to the lead content of the liquid nutrient. That is, if a nutrient contains a few micrograms per milliliter of lead or cadmium ion, then the plant tissue on a dry weight basis will contain a few micrograms per gram. On the other hand, if a soil is treated with a clay containing lead, or even with an insoluble form of lead such as lead sulfide, then the plant tissues can take up much more lead than would be indicated by the lead content of the soil moisture (4). This can be attributed to the solubilizing properties of the organic substances exuded by the growing plant roots. This root exudate can be shown to consist of a complex mixture of chemical compounds including such materials as sugars, phenols, and proteins which evidently are localized and concentrated in the soil system whereas they are diluted in the hydroponic system. In addition, soil bacteria can break down insoluble salts such as sulfides, thus releasing the heavy metal for plant uptake.

It is dangerous to generalize too quickly about the behavior of trace metals based on simple chemical analogies, because the biochemical mechanisms may be greatly different. To illustrate this point, we might contrast the behavior of lead and cadmium in relation to plant uptake (5). These two metals are taken up in comparable amounts from hydroponic cultures of corn plants, insofar as comparisons of stalks or leaves are concerned. On the other hand, if the roots are analyzed, then we see a marked contrast. While both elements are concentrated in the roots, the degree of concentration is very much more pronounced for lead than for cadmium. For example, a hydroponic culture of corn roots shows an accumulation up to 3,000 ppm of lead and 200 ppm of cadmium in the roots when both were grown in solutions containing 20 ppm. It is found that the bulk of the lead, perhaps 90 to 95 percent, can be readily extracted from the intact root system by washing with a complexing agent such as EDTA. A less efficient washing can be achieved with a calcium nitrate solution. The lead is largely contained on the outside rather than within the interior of the root system. The root membrane seems to represent a first line of defense against the entry of lead into the plant. The exact form of the lead on the surfaces of the roots is still unknown. It may be considered as being ion exchanged but some recent evidence from electron microscopy suggests the presence of small nodules that are localized in character (6).

Another point of difference between lead and cadmium is in the solubility of phosphates. Since phosphates are naturally occurring constituents of all living cells, it might be natural to expect the precipitation of lead phosphate within cell tissues. Indeed we have found some evidence for such precipitation through scanning electron microscopy of plant tissues containing relatively high concentrations of lead. Incidentally, the first symptoms of lead poisoning in a plant, as far as the plant physiologist is concerned, is a leaf discoloration and curl characteristics of phosphate deficiency. At the present time there is still some uncertainty as to the precise form of the phosphate. It has been known for several years that if lead acetate solutions are applied to plant cells, a localized precipitation of lead phosphate as lead hydroxyapatite or hydroxyorthophosphate, $Pb_5(PO_4)_3OH$, is observed. A report, as yet unverified, of the possible formation of lead pyrophosphate, presumably arising through the interaction of lead ion with pyrophosphate which is known to be an intermediate in phosphate metabolism, has appeared (7). Once the trace metal enters the plant system in soluble form, it is rapidly translocated through the plant. Apparently certain metals are strongly bonded at membrane walls both in plant and animal cells. Whether this might be regarded as a protective mechanism or as an adverse effect, depends upon the nature and function of the membrane.

Whether heavy metals can enter plants directly from airborne particulates has not been clearly established. Some authorities maintain that such particles have no effects, apart from the possible blockage of stomata of leaves, while others point to the fact that it is impossible to wash all traces of metals, such as lead, from the surfaces of leaves even with detergents or complexing agents. Detailed examination of plant leaves by techniques such as scanning electron microscopy should help to resolve this question.

The entry of trace metals into the animal organism can be through two principal routes, through ingestion of food and water and through the respiratory system. Experimental evidence indicates that ingested lead is taken up quite inefficiently by the human body, perhaps to the extent of 10 percent. The reason for this low uptake has never been stated, but it would appear that if the body has a defense mechanism against the absorption of lead from the intestine, there may be a disease corresponding to the breakdown of this mechanism. Clearly, a detailed study is needed. Lead breathed in as particulate matter is much more efficiently absorbed, so that some authorities feel that these two sources might be of the same order of magnitude even though the intake through food represents a much greater amount. In the blood stream, perhaps 95 percent of the lead is associated with the red corpuscles and only 5 percent with the blood serum. The blood presumably represents the medium by which lead is transported into the various organs, but the quantitative rate law is unknown.

It is known that the skeleton represents a depository, from which lead is only partially extractable and presumably only under severe conditions such as treatment with chelating agents. It is also known that lead forms special nodules in kidney tissue, and it has been inferred that these nodules are insoluble lead protein complexes. Cadmium also concentrates in the kidneys but because the protein complexes of cadmium are more soluble, they do not form the same type of nodules. Cadmium has a pronounced effect upon the blood pressure, presumably through its action upon the kidneys.

Children appear to be much more susceptible to nerve damage and brain damage by lead poisoning than do adults. The reason is not at all clear, and therefore it appears to be difficult to assign a threshold level of blood lead content below which no damage can be detected. Some authorities, notably Kehoe, have regarded 80 micrograms per 100 milliliters as a safe limit, whereas other authorities have felt that 40 micrograms or even 36 might be more realistic and safer limits (8). Where we draw the line makes a great deal of difference, because most children exhibiting 80 micrograms of blood lead and showing symptoms of poisoning have been demonstrably exposed to sources such as paints. On the other hand, 15 to 20 percent of children in clinical tests in downstate Illinois have shown blood lead contents over 40 micrograms (9). Authorities in England have recently placed much more stress on the possibility of lead from automotive fuels representing an important contribution to the poisoning of children than have authorities in this country (8).

When we attempt to describe the effects of trace metals in biochemical terms, we are confronted with more ignorance than knowledge.

Biological effects of trace metals can be described at various organizational levels, namely: the organism or whole plant or animal, the organ, the cell, the organelle, the membrane, and finally the molecular level. As we proceed down the organizational scale, the depth of our ignorance increases except that finally at the molecular or enzymatic level once more we find some positive knowledge. Clinical studies on lead poisoning reveal effects like mental retardation and disturbances of the nervous system at the organism level. Concentrations in certain organs, for example the kidney, are well established. At the cellular level, interference with the energy-conversion process have been established, and this can be traced to the subcellular, or organelle level, in that isolated mitochondria both from plant and animal cells show the toxic effects. When we reach the membrane level, we find references to preferential binding, but little detail as to the mechanism of the binding, or effects on transport rates through the membrane. At the molecular level, we find vague references to the binding of metals to sulfhydryl groups of enzyme systems and speculations as to the relative effects of metals based on the stabilities of sulfhydryl-containing chelates, but little that is solid and well established. I am generalizing here, and referring to toxicity and not to specific biochemical systems, such as hemoglobin, vitamin B_{12} and chlorophyll, which involve trace metals in well defined roles.

Among the areas requiring further research are the protective mechanisms for trace metals especially among the higher organisms, both plant and animal. These protective mechanisms could include such phenomena as preferential binding to membrane surfaces, precipitation as inorganic salts or organic derivatives, complexation by biological chelating agents, etc. An almost completely unexplored area is the question of the combined effects of two or more trace metals. Are the effects additive, competitive, or synergistic? If each metal taken separately has a certain tolerance level, what is the tolerance level for a mixture of two metals? Are the protective mechanisms for two or more metals independent of one another?

In summary, a great deal of comprehensive work is needed on the effects of trace metals on the total environment. This work must consider both extremes and all intermediate organizational levels, and it must consider the interactions among the trace elements as well as their individual effects. Both the short-term and long-term effects need consideration. By long-term, I mean a time period commensurate with the life span of the entity under consideration. If we are dealing with human beings, this means a period of the order of a century, but if we are dealing with cells, it might be a much shorter period. If we are considering effects to mankind as a species, we need to look at truly long-term effects, over time spans of hundreds or thousands of years.

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SESSION II
TRANSPORT AND EFFECTS

Chairman:

H. Wiser
U. S. Environmental Protection Agency

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PHYSICAL TRANSPORT OF TRACE METALS IN THE LAKE WASHINGTON WATERSHED

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INTRODUCTION

The biogeochemical cycle removes material from the lithosphere, redistributes it throughout the atmosphere and hydrosphere and ultimately reincorporates it into the lithosphere. This continuous cyclic process includes weathering, erosion, transport, and deposition. The transfer rates and amounts of material participating in this cycle can be accelerated, for example, by poor land management practices, or by increasing the input of material as byproducts of technological developments. By this latter means man has introduced quantities of trace metals into the environment. These trace metals are frequently transported easily and are injected directly into the major transport pathways of the environment. The amount of increase of these trace metals in a specific environment can be measured in recent sediment profiles where the time history of deposition can be established.

Geochemical Cycle

The geochemical cycle consists of source, transport, and sink. The natural source of trace metals is the lithosphere; artificial sources have been created by industrialization and urbanization; transport occurs by wind, water and ice; the sinks are fresh water lakes, rivers or the oceans. The most significant modes of trace metal transport are by wind and water as shown in Table 1, where amounts of heavy metals produced and the potential transport to the ocean are given.

The removal of trace metals to a geochemical sink must include an aqueous phase. Removal processes occurring can include absorption, precipitation, oxidation, reduction, and complex formation. Because of the rapid removal processes, in general, many trace metals are lost from the aquatic environment within a short distance from the initial input (1, 2). The concentrations of trace metals in water are low and were

TABLE 1 GLOBAL TRACE METAL PRODUCTION AND POTENTIAL OCEAN INPUT*

Element	Mining production (10^6 tons/yr)	Transport by rivers to oceans (10^6 tons/yr)	Atmospheric washout (10^6 tons/yr)	Ratio aeolian/ fluvial
Pb	3	0.1	0.3	3.0
Cu	6	0.25	0.2	0.8
V	0.02	0.03	0.02	0.7
Ni	0.5	0.01	0.03	3.0
Cr	2	0.04	0.02	0.5
Sn	0.2	0.002	0.03	15
Cd	0.01	0.0005	0.01	20
Hg	0.009	0.003	0.08	27

*Reference 3.

difficult to measure until recent improvements were made in analytical techniques. The analytical difficulties of the past have contributed to the limited understanding of the geochemical cycle of many trace elements. It is through a greater understanding of the geochemical cycling of trace metals that insight can be gained on problems of pollutants in the aquatic environment.

Modes of Physical Transport

The major modes of physical transport are advection and diffusion. The advective processes are by far the most important in the transport of most trace metals in the atmosphere or hydrosphere on a global scale. For certain volatile trace elements such as mercury, the diffusion process from the lithosphere would dominate.

Three modes of advective transport of trace metals are (a) that which is carried by the wind (aeolian), (b) that which is carried by running water either suspended or dissolved (fluvial), and (c) that which is removed or transported by rain or other forms of precipitation scavenging (pluvial). The settling of particles under the influence of gravity is a major mode of vertical transport.

Aeolian transport was noted as early as the 12th century (4). Meridional and zonal dust transport have been observed from the Sahara to the mid-European continent (5), and from Africa to the Caribbean (6), volcanic eruptions such as Krakatoa spread volcanic dust worldwide. Radioactive fallout originating from Eniwetok, Bikini, and Novya Zemyla, USSR, and Lop Nor, China, has been followed around the world. These sources have served as tracers of geochemical processes and have permitted calculations of residence times and transit times in the atmosphere to be made (7–10); the input of the radioactive tracers into the hydrosphere has permitted similar calculations to be made in the oceans and freshwater areas (11–13). The recent findings on the build up of lead and mercury in Greenland ice profiles illustrate long range aeolian transport of these trace metals (14, 15). High concentrations of trace metals in surface air of North American cities indicates that short range aeolian transport is considerable (16). Significant quantities of iron, zinc, arsenic, silver, antimony, cobalt and mercury were found near Toronto (17); in the Chicago area concentrations in excess of 10^{-9} g/m^3 were found for iron, zinc, manganese, vanadium, antimony, chromium, mercury, aluminum, cerium, silver, and selenium (18).

It is apparent that the trace metal input to the atmosphere and hydrosphere follows the transport processes of the geochemical cycle. The problem arising from local pollution sources of trace metals may be exported thousands of kilometers from the point of origin. The pollution from industrialized nations then becomes an international concern. It is clear that effective control of potential trace metal pollutants can be exercised only at the source where the quantity and chemical form can be regulated.

Sediment Method

The evaluation of contemporary transport and distribution of trace metals in a given region can be achieved by systematic collection and analysis of air and water samples, dry fallout, precipitation, soils and sediments. While this comprehensive technique is satisfactory for evaluating contemporary events, it cannot determine the history of trace metals in a given region. To determine the history of trace metal build up in a given region, soil and sediment profiles are most suitable. Because of weathering, natural mixing, and disruption by human activities, undisturbed soil profiles are difficult to obtain. However, sediment cores often are uniquely suited for the preservation of the trace metals history.

Sediment cores for trace metals have the following advantages:

1. relatively independent from weathering,
2. sedimentary deposits, in general, increase at a fairly constant rate per year,
3. sedimentary material serves as scavengers for trace metals,
4. usually are outside the sphere of human modification but frequently contain an anthropogenic anomaly that can be specifically dated.

Two basic assumptions are necessary in using sediment

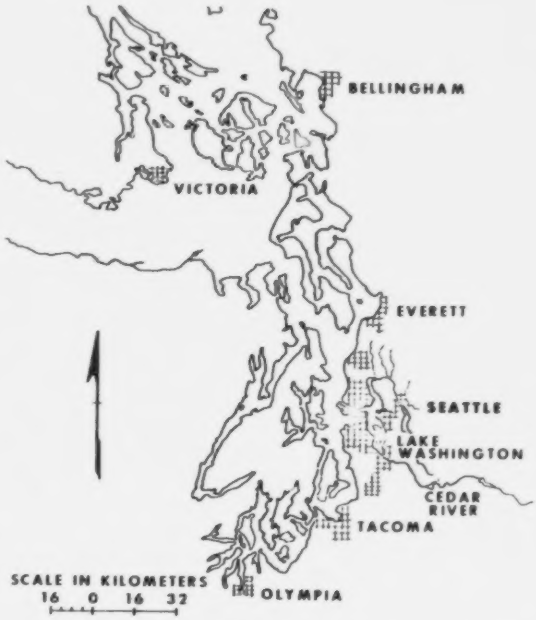

Figure 1. Puget Sound basin.

cores for the trace metal history; first, the system must be closed to gains and losses of the trace metal at all levels in the core and second, a sequential accumulation must have taken place. Since the man-made increase in trace elements has occurred in recent years, it is essential to have time resolution to within a few years. Practically, this demands a sedimentation rate of greater than about two mm/yr.

The application of sediment cores to the time history of trace metals in Lake Washington has been made. Figure 1 shows the Lake Washington area and the major drainage basin, the Cedar River. The urban and suburban development of the region has been increasing rapidly since about 1940. Lake Washington has an area of 88 km^2 and a mean depth of 33 meters. The City of Seattle lies along the western shore with suburban development surrounding the lake. It is spanned by two floating bridges completed in 1941 and 1963. A ship canal and locks were built in 1916 which connected the lake with Lake Union and Puget Sound. This lowered the lake some 3 m to its current elevation of 4.3 m above mean sea level. To maintain sufficient flow of water to operate the locks, the Cedar River, with an average flow of 19 m^3/sec, was permanently diverted into the southern end of the lake in 1916.

The lake has a history of cultural eutrophication (19) but little direct industrial waste discharge is believed to have occurred. Recovery from cultural eutrophication has been rapid since 1968 (20). The City of Renton is located on the Cedar River where Boeing and Pacific Car and Foundry plants are potential major industrial sources of trace metals.

RESULTS AND DISCUSSION

Mercury

The core locations for sampling trace metals are shown in Figure 2. The mercury profiles for the three cores taken are shown in Figure 3. The magnitude of local variations is shown by duplicate cores from station 2; the absolute concentrations are initially 60 percent different at the surface. A fixed point in time has been found at the 18 cm level at station 2 (21) and 25 cm at station 4 when the Lake Washington Ship Canal and Government Locks were constructed. A silt band was produced when the lake level was lowered three m and the Cedar River diversion was completed in 1916. On this basis the sediment rate was found to be 3.3 mm/yr for station 2 in agreement with reported values at a nearby location (21). For station 4, by a fitting of the similar mercury structure, and the silt layer, a sedimentation rate of 4.4 mm/yr is indicated. This is consistent with the core location which was closer to the Cedar River, a major source of sediment material.

The discrepancy between stations is in the absolute magnitude of the mercury concentration. The similarity in profiles indicates that general lake conditions are being reflected. It is apparent that the mercury associated with the larger sedimentation rate has a lower concentration; the total mercury available to the sediment, however, can be constant. The dilution by low mercury sediment could account for the discrepancy between the cores from station 4 and station 2. The difference in sediment rate is ca. 33 percent, whereas the differences in absolute concentrations is ca. 50 percent, and probably within the error of the sampling and analysis. The source of mercury to the sediments must be dispersed throughout the lake. This would indicate that the mercury is being transported either by aeolian processes or that the mercury in the lake is added at about the same rate throughout. The dramatic decrease at 4 to 6 cm for all elements represents what is believed to be redistribution of silt due to the construction of the second floating bridge, completed in 1963. These core section samples had high silica content in contrast to the other samples. The X-ray radiographs of cores taken nearby show a density anomaly at the same depth which could be attributed to the bridge construction (21). Additional cores have been taken to attempt to define local and areal distribution of the mercury input.

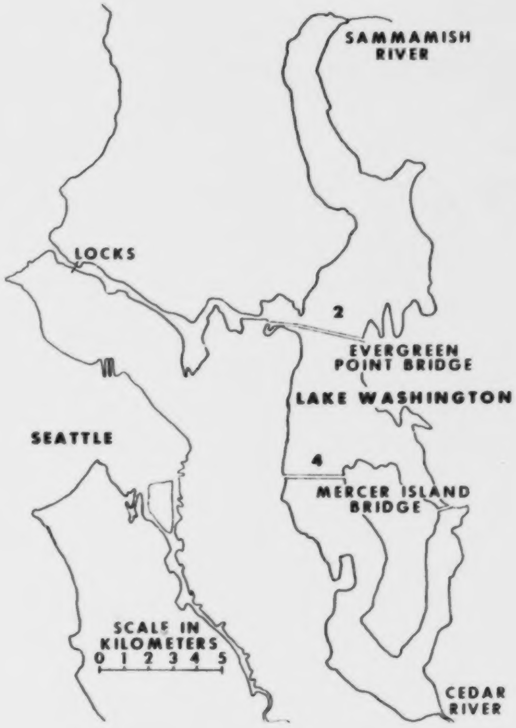

Figure 2. Lake Washington core sampling locations.

At the present time it is not possible to separate out the several suspected sources which contribute to the mercury budget of the lake. Suspected sources for mercury include: combustion of fossil fuels, especially coal; aeolian and aeolian-fluvial transport from the Tacoma smelter; municipal sewage or treated effluents; local industrial or domestic sources such as mercury in marine paints, fungicides, etc. The mercury associated with sewage wastes and storm runoff should be

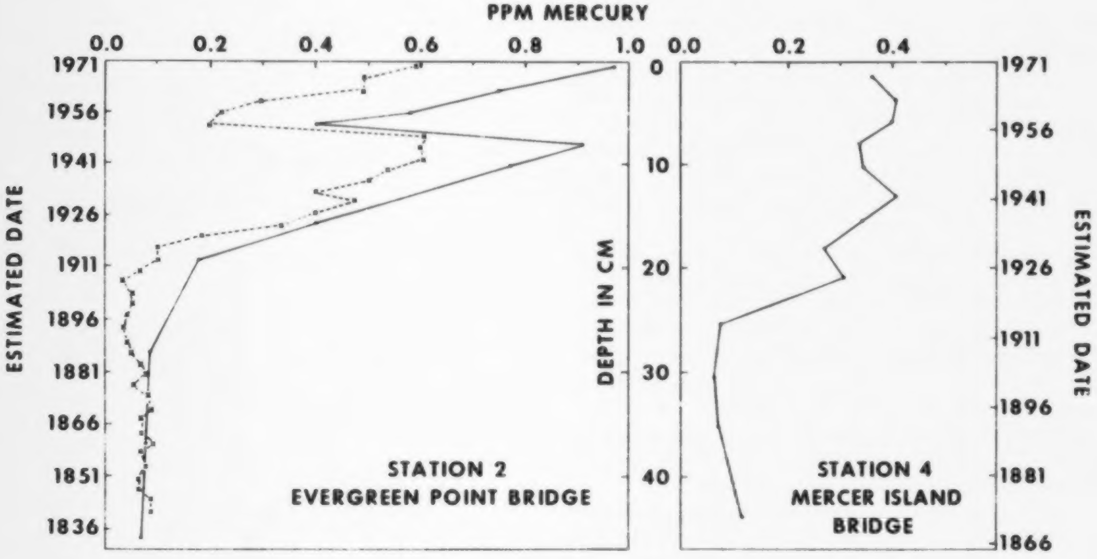

Figure 3. Mercury in Lake Washington cores.

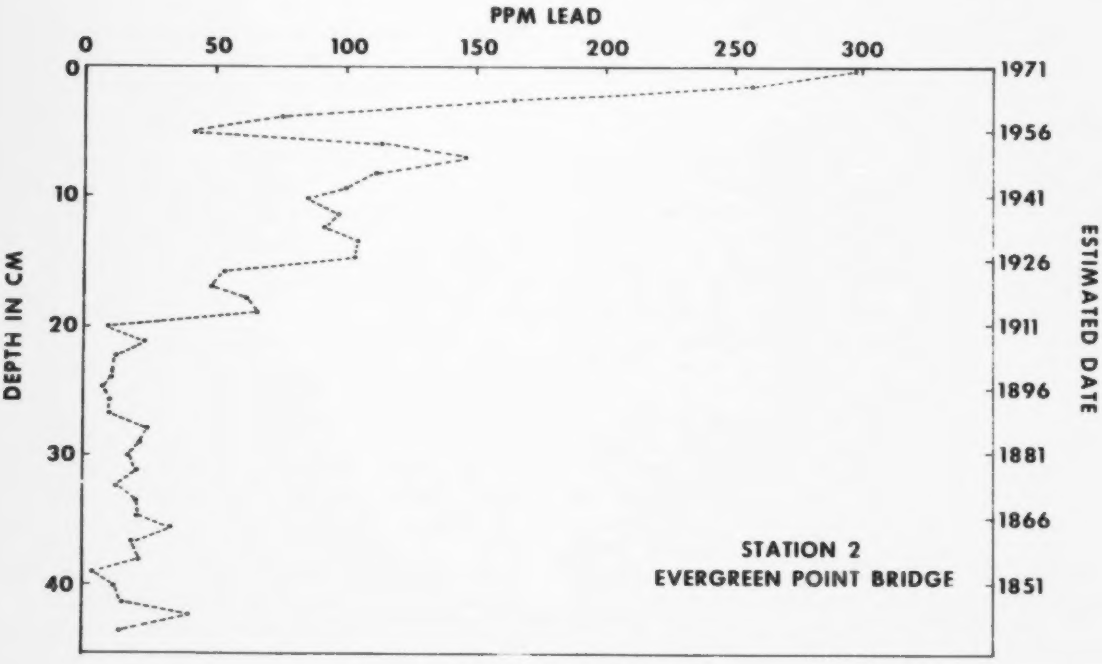

Figure 4. Lead in Lake Washington core.

diminishing now following the diversion of sewage from the lake in 1968.

Lead

The lead profile is shown in Figure 4 for a core from station 2. The gross structure of the lead concentration is similar to the mercury core with the increase starting at the 18 cm level. The lead content is shown to increase by about a factor of 16 from the base line prior to 1916. The present sediment concentration of about 300 ppm indicates a continuous and increasing input source. The doubling time for the increase in lead concentration is about 18 years.

The fine structure of the core can be related to specific events by assuming the sedimentation rate of 3.3 mm/yr and no migration of the lead after deposition. The initial increase from base line at 18 to 20 cm depth can be ascribed to the diversion of the Cedar River. The Cedar River drainage basin is about 500 km^2 in area and is generally downwind (E–NE) of a potential source, the American Smelting and Refining Company Smelter, in Tacoma. This smelter has been in operation since 1890 and processed ore mainly for lead from 1890 to 1913; current stack emissions may be as much as 40 percent lead oxide. (22). Aeolian transport would bring lead to the drainage basin and then by fluvial transport into the lake via the Cedar River. The second rapid increase at the 14 to 15 cm level would correspond to the 1920's when lead alkyls were introduced in gasoline. The decrease in the lead deposition from the 14 to 9 cm levels would correspond to the depression and war years. The use of gasoline engines, predominately in the automobile, may be directly related to the lead profile. The 9 to 0 cm level represents the post war period when automobile use had increased rapidly with a corresponding increase in lead concentrations.

The concentration of lead is increasing at a rapid rate in the sediment core. It is possible that the proximity of the station to the bridge, 400 m to the south, may be responsible for the high concentrations measured. Additional core samples taken recently should better define the local and areal distribution of lead in Lake Washington sediments.

Zinc and Copper

The zinc and copper concentration profiles shown in Figure 5 are similar to those of mercury and lead. The rapid increase in concentration of zinc occurred at about the 16 to 17 cm level with the characteristic minimum at the 6 cm level shown in both zinc and copper. Zinc and copper concentrations have increased by about a factor of four over the base line values prior to 1916. The present concentrations for zinc at 230 ppm and copper at 50 ppm have not increased much since 1950.

The sources of zinc and copper to the lake include natural mineral deposits in the Cedar River watershed, aeolian transport from the smelter in Tacoma and domestic and industrial uses of zinc and copper in algicides, pesticides, paint, galvanized steel.

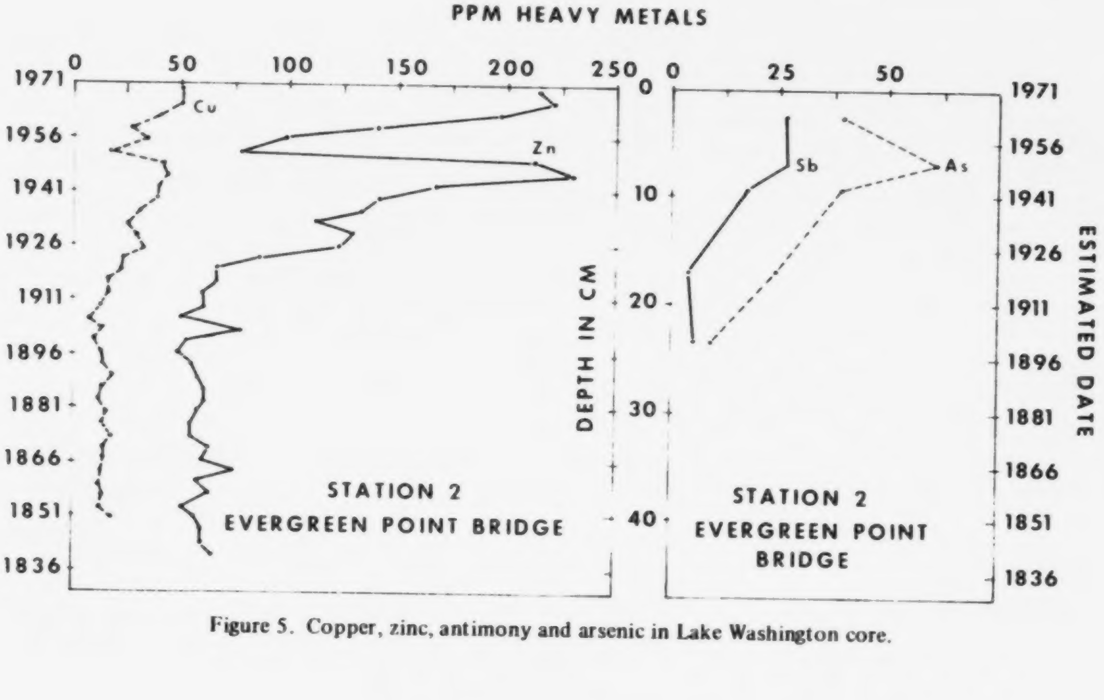

Figure 5. Copper, zinc, antimony and arsenic in Lake Washington core.

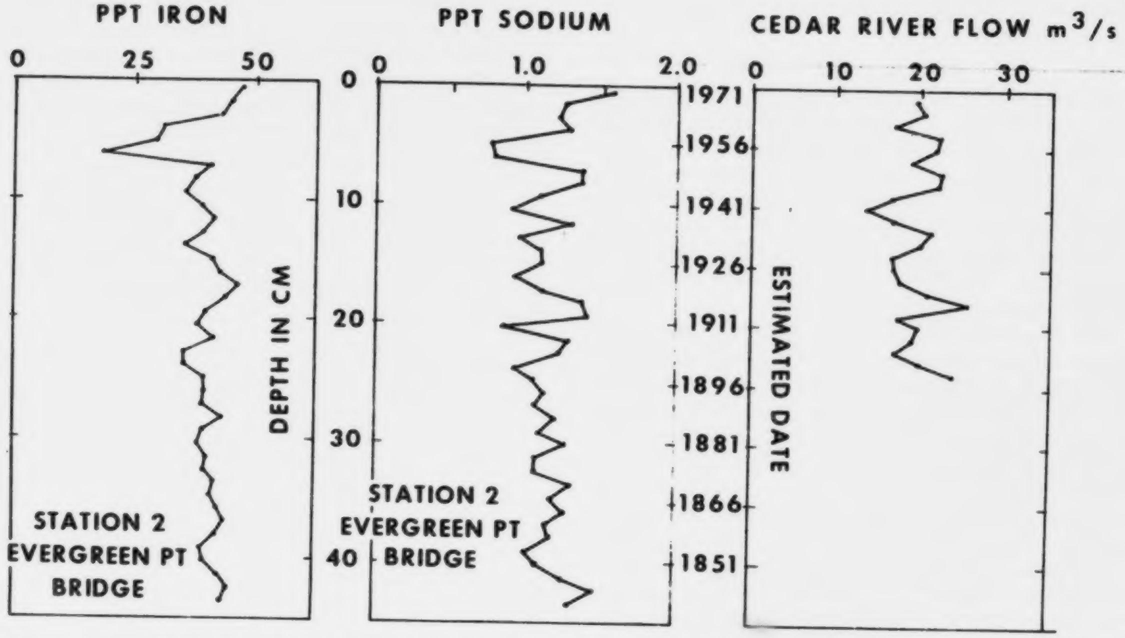

Figure 6. Iron and sodium in Lake Washington core; Cedar River annual discharge averaged over 3-year increments.

Arsenic and Antimony

The few data points for arsenic and antimony are shown in Figure 5 measured by neutron activation analysis. The locations in the core were selected after the other trace metals were analyzed to observe if these elements were following the same pattern. The same general pattern of concentrations was followed. Migration of the arsenic from a fixed point of deposition could occur since a volatile arsenic compound, AsH_3, could be formed in the reducing environment of the sediment. This elemental migration does not appear to be taking place at a rapid rate which would perturb the profile concentrations. By inference, the mercury migration should be low, indicating that the elements studied, which have been deposited in the lake sediments, do not migrate at a significant rate. A more detailed profile is needed for arsenic and antimony, especially in the upper layers.

The increase from natural background prior to 1916 has been about five times for arsenic and antimony. The sources for these trace metals are probably aeolian transport from the smelter in Tacoma. The arsenic concentration increase may also be from the municipal sewage where herbicides and insecticides have been used extensively on gardens, and from arsenic contained in detergents.

Iron and Sodium

The iron and sodium profiles are shown in Figure 6. Since these elements are major constituents of the erosion process, the concentration, as a function of time (depth), indicates differences caused by natural changes in the watershed, which drains into the lake. The profile shows fluctuations around a mean value of about 40 ppt iron and 1.2 ppt sodium. There is no apparent long term trend in the concentrations of sodium and iron in the sediment data, in contrast to trends of the other trace metals measured. The minimum at the 6 cm level is again evident and for both metals. There appears to be a slight increase at the 16 to 18 cm level when the lake level was lowered and the Cedar River diversion was completed.

The erosion rate depends on the rainfall and should

TABLE 2 REPRESENTATIVE TRACE METAL CONCENTRATIONS IN LAKE WASHINGTON IN, mg/liter

Element	Average fluvial input	Average fluvial output	Observed range in lake
Fe	0.055	0.033	0.010–0.095
Na	3.43	4.70	4.45–5.00
Pb	0.0009	0.00085	0.0003–0.0012
Zn	0.026	0.023	0.004–0.047
Cu	0.0025	0.003	0.0011–0.0079
Hg	0.00005	0.00005	0.000008–0.000068

correlate with runoff. Figure 6 shows the general correlation of iron and sodium concentrations with the Cedar River discharge, using the discharge as a measure of total watershed runoff. A study of post-glacial lake sediments in Northern England showed that the relative concentrations of alkalai metal elements in sediment was related directly to the intensity of erosion, for example, rainfall in the drainage basin (23). Under rapid erosion conditions less sodium, for example, was leached from the soil particles and proportionately more was carried by the sediment load for deposition into the lake. Similarly, in the Lake Washington drainage basin high rainfall and subsequent high runoff produced sediments with high sodium concentrations.

This same process should occur for other macro-constituents of the sediment such as iron and manganese. However, unlike sodium, chemical and biological reactions can release these metals in the sediment under certain pH and redox conditions. These conditions do not appear to be occurring in the Lake Washington sediments.

Budget

The transport of trace metals to the lake is reflected in the core profiles. Iron and sodium, for example, correlate with the discharges of the Cedar River, indicative of fluvial transport. The modes of transport for the other trace metals are not evident from the core profiles alone, but require geochemical budget calculations to indicate the relative importance of wind and water processes. The preliminary data on measurements, by atomic absorption spectrometry, of trace metal concentrations are shown in Table 2. Fluvial input data were obtained from the Cedar River and Sammamish River inlets to the lake, while the outlet data were obtained from stations in the lake near the eastern end of the ship canal.

The budget calculation method has simplified the geochemical system into: fluvial and aeolian inputs, a sedimentary sink, and fluvial output. The aeolian input of trace metals was assumed to be relatively insoluble (24). The complex processes of redistribution within the lake were neglected in this first approximation since only input and output were needed in the budget computations.

The input and output concentrations indicate that, with the exception of sodium and iron, the trace metal concentration in the water is not greatly changed by passage through the lake. The data shown in Table 3 are based on an average inflow of 1.17 x 10^9 m^3/per year with an incoming sediment load of 50 x 10^6 kg/per year (25) and the data from Table 2; it is assumed that the incoming sediment has a composition representative of crustal materials. The aeolian input was estimated by subtracting the net fluvial input from the annual sediment input. An independent check of the input of iron and sodium by aeolian transport, using dustfall data, indicates that the estimated aeolian values are probably high by a factor of four, on the basis of net transport. This is not considered a serious error for sodium because of the large magnitude of the numbers involved. The discrepancy in iron is probably due to insufficient iron data; since iron is both biologically and chemically active in the aqueous environment, adequate sampling is difficult.

In contrast to iron and sodium, the heavy metals show very different transport effects. While the annual fluvial input is approximately equal to the amount deposited in the sediments for zinc, copper, and mercury, the net fluvial transport, input-output, retained in the lake sediments amounts to only 32 percent, 44 percent, and 7 percent, respectively. This indicates substantial aeolion contributions for all these metals. The aeolian transport

TABLE 3 TRACE METAL BUDGET FOR LAKE WASHINGTON

Elements	Annual transport				Annual deposition in sediments (measured)
	Input	Fluvial output	Net	Aeolian input	
Fe, tons	2570	40	2530	2200*	4700
Na, tons	5420	5440	(−) 20	180†	160
Pb, tons	1.3	1	0.3	29.8	30
Zn, tons	34	27	7	15	22
Cu, tons	5.7	3.5	2.2	2.8	5
Hg, kg	62	58	4	56	60

*Based on an average dustfall for Seattle (26) of 38.92 U. S. tons/mi^2/mon = 14.8 x 10^6 kg/yr over Lake Washington, and using an average iron concentration of 3400 ppm for urban dust (18), the iron input due to aeolian transport would be on the order of 500 tons/yr.

†Based on (*) above, Na input is 45 tons/yr from aeolian transport; even if a higher Na concentration is assumed because of marine aerosols, the aeolian component is still very small compared to the fluvial.

for lead is even more striking; just considering the input, about 10 times as much lead enters the lake from the air as by fluvial means. Using lead concentrations in dustfall for Seattle (26), the input from the atmosphere to the lake is estimated to be 24,000 kg/per year, which is in good agreement with the estimated atmospheric contribution of 29,750 kg/per year.

Another way of approaching these input calculations is to consider the nature of the trace metal enrichment in the sediments since 1916. Table 4 shows the enrichment in the contemporary surface sediment relative to the pre-1916 sediment. Table 5 shows the contemporary aeolian input of heavy metals to the sediments, as estimated from the enrichment of these metals in the present sediment, assuming that the enrichment since 1916 is due entirely to aeolian material. This estimate is compared to that for aeolian input, as derived from the net transport budget in Table 3. The results are striking for lead and mercury in particular, where both methods of calculation indicate a very high aeolian component. Copper and zinc also show substantial aeolian contributions, but the percentages are not as large as those of mercury and lead, reflecting the higher natural backgrounds of copper and zinc in the core.

TABLE 4 TRACE METAL ENRICHMENT IN LAKE WASHINGTON SEDIMENTS SINCE 1916

Element	Enrichment ratio 1971/pre-1916
Fe	1
Na	1
Pb	16.6
Zn	3.9
Cu	3.6
Hg	10.0

Based on the lake volume, fluvial output and sedimentary deposition, the following mean residence times were estimated: iron, 11 days; lead, 26 days; mercury, 15 months; copper, 16 months; zinc, 21 months; and sodium, 29 months. The mean residence time for the lake water is also 29 months. Such figures must be considered very rough approximations, as the assumption of complete mixing time, being much less than the mean residence time, does not appear valid during periods of stratification, June to October, at least for iron and lead; nevertheless, the ordering of mean residence times Fe $<$ Pb $<$ Hg $<$ Cu $<$ Zn $<$ Na is identical to those estimated for these trace metals in the ocean (27).

There is evidence that the trace metals are primarily transported in the suspended load, often in inert positions within the suspended particles (28). A further observation is that much of the detrital trace metals never leave the solid phase from initial rock weathering to detrital deposition. This is demonstrated by the Lake Washington sediments, where the trace element composition more nearly reflects that of the crustal materials in the suspended load, rather than that of the incoming water. Lead, entering the lake from the atmosphere, appears to have a very short residence time in the water column, as shown by the low concentrations measured in the water, and by mean residence time estimates. It is suspected that the same is true for other heavy metals in atmospheric material, but our data can not confirm this.

TABLE 5 PERCENTAGE OF CURRENT HEAVY METAL INPUT TO LAKE WASHINGTON SEDIMENTS ATTRIBUTED TO AEOLIAN PROCESSES AS ESTIMATED FROM TRACE METAL ENRICHMENT AND BUDGET DATA

Element	Contemporary aeolian input to sediment	
	Enrichment*	Budget†
Pb	94%	99%
Zn	74%	68%
Cu	72%	56%
Hg	91%	93%

*Assuming that all the heavy metal enrichment since 1916 is due to aeolian transport.

†On a net transport basis.

SUMMARY

In the Lake Washington drainage, trace metal enrichment appears to be correlated with the cultural development of the region, and is brought into the local hydrosphere principally by advective atmospheric transport. Fluvial processes are of considerable significance, but appear to be reflected in the sediments primarily on the basis of the suspended load. It has been found that trace metal analysis of recent lake sediments can provide meaningful data concerning the impact of man on his environment, and offers a unique opportunity for evaluating past environmental conditions.

ACKNOWLEDGMENT

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BIOLOGICAL UPTAKE AND DISTRIBUTION OF LEAD IN ANIMALS*

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The widespread use and distribution of heavy metals and other contaminants in the environment have created the need for the development of models that are able to predict the uptake, accumulation and distribution of these contaminants in living organisms. These models, when coupled with studies on effects and alterations that these contaminants might inflict on the environment and its components, become extremely valuable to the decision maker.

Part of the effort undertaken by the interdisciplinary study of heavy metals, currently taking place at the University of Illinois under grant from the National Science Foundation, is to develop predictive models for heavy metals in general, and lead in particular. This paper will present a model that has been developed in the modeling team of the heavy metal study. The basic concepts of the model are general enough to make them applicable to many biological uptake and retention phenomenas. The model belongs to a class, usually, known as compartmental models or, more specifically, first order linear models. The first order assumption, in the studies of biological uptake and accumulation, was suggested for radionuclides and other heavy metals by the International Commission on Radiological Protection (1). Many models of this type have been developed for a variety of purposes, ranging from milk contamination in cows by radionuclides (2, 3), to DDT accumulation (4), to retention of ingested elements by animals (5).

The following model is a multi-compartment, first order linear model to study the uptake, retention, and elimination of heavy metals by animals. Conceptually, it is applicable to all mammals and most contaminants. The body is divided into as many organs of interest as desired, and different types of input are considered. The main emphasis here will be on lead. The basic assumptions of the model are:

1. The transfer of the contaminant, namely lead, within the animal is accomplished via the blood.
2. The uptake and elimination of the contaminant follow a first order law. This implies that the instantaneous transfer rate from any given organ is directly proportional to the amount present in the organ.

Mass equilibrium is satisfied at any given organ, and for the body as a whole.

Figure 1 shows a schematic diagram of the physical flow of lead within the body. In this particular model, two types of input are considered. The lead from air via respiration, and the lead ingested with food and water. Other possible modes are neglected. Three types of output are also considered. These are the output via the urine, feces, and lead exhaled. Other means of output are neglected.

The conceptual or compartmental model corresponding to Figure 1 is shown in Figure 2. In this particular abstraction, the function of an organ is separated from its physical entity. The concentration of lead in the urine is assumed, here, to be proportional to the concentration of lead in the blood rather than the concentration of lead in the tissue of the kidney. Other interpretations could be used. The mathematical model describing the uptake and elimination of lead, as derived from Figure 2, is given by a set of first order linear differential equations with constant parameters. Each equation satisfies equilibrium at a given organ. Each equation states that the rate of change in accumulation within a given organ, is equal to the uptake rate minus, the elimination rate.

The input rates to the system

$$R_{air} = (BR) \cdot (CA) \cdot (X_A) \qquad (1)$$

$$R'_{fd} = \sum_{n=1}^{N} (IR_n) \cdot (CE_n) \cdot (X_n) \qquad (2)$$

---

*Sponsored by National Science Foundation, NSF IRRPOS GRANT GI-26 and NSF RANN GRANT GI-31605.

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The output rates from the system are given as

$$FE = \lambda_f^1 \cdot (BL) + (R_{fd} - R_{fd}^1)$$

$$FE = \lambda_f^1 \cdot (BL) + \sum_{n=1}^{N} (CE_n) \cdot (I_n) \cdot (1 - X_n) \qquad (3)$$

$$UR = \lambda_u^1 \, (BL) \qquad (4)$$

The equilibrium equations describing the behaviour of the system are:

$$\frac{d(KI)}{dt} = -\lambda_{KI} \cdot (KI) + \lambda^1{}_{KI} \cdot (BL) \qquad (5)$$

$$\frac{d(L)}{dt} = -\lambda_L \cdot (L) + \lambda^1{}_L \cdot (BL) \qquad (6)$$

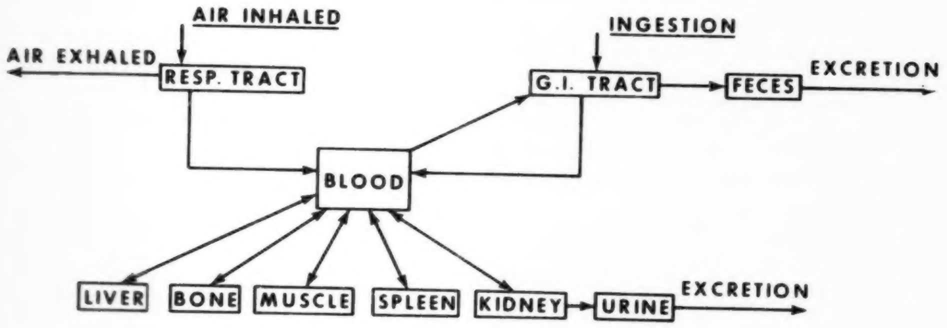
$$\frac{d(BO)}{dt} = -\lambda_{BO} \cdot (BO) + \lambda^1{}_{BO} \cdot (BL) \qquad (7)$$

$$\frac{d(M)}{dt} = -\lambda_M \cdot (M) + \lambda^1{}_M \cdot (BL) \qquad (8)$$

$$\frac{d(SP)}{dt} = -\lambda_{SP} \cdot (SP) + \lambda^1{}_{SP} \cdot (BL) \qquad (9)$$

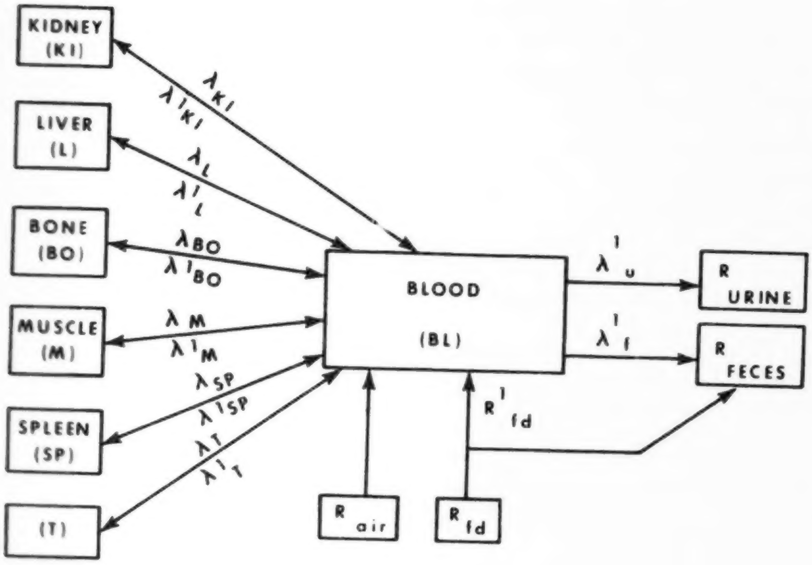
$$\frac{d(T)}{dt} = -\lambda_T \cdot (T) + \lambda^1{}_T \cdot (BL) \qquad (10)$$

$$\frac{d(BL)}{dt} = - \frac{d(KI)}{dt} - \frac{d(L)}{dt} - \frac{d(BO)}{dt} - \frac{d(M)}{dt} - \frac{d(SP)}{dt} - \frac{d(T)}{dt} \qquad (11)$$
$$+ R_{air} + R^1{}_{fd} - \lambda^1{}_u \, (BL) - \lambda^1{}_f \, (BL)$$



AIR INHALED
AIR EXHALED
RESP. TRACT
INGESTION
G.I. TRACT
FECES
EXCRETION
BLOOD
LIVER
BONE
MUSCLE
SPLEEN
KIDNEY
URINE
EXCRETION

Figure 1. Schematic of physical flow of lead in the body.



KIDNEY (KI)
LIVER (L)
BONE (BO)
MUSCLE (M)
SPLEEN (SP)
(T)
λ KI
λ' KI
λ L
λ' L
λ BO
λ' BO
λ M
λ' M
λ SP
λ' SP
λ T
λ' T
BLOOD (BL)
λ' u
λ' f
R URINE
R FECES
R' fd
R air
R fd

Figure 2. Compartmental model of flow of lead in body.

Where:

KI, L, BO, M, SP, BL represent the amount of lead, respectively, in the Kidney, Liver, Bone, Muscle, Spleen, and Blood.

T represents the amount of lead in all other tissues, organs, and sinks not included in the model. The inclusion of this conceptual organ allows the conservation of equilibrium in the whole system.

UR, FE represent the amount of lead respectively in the urine and feces.

λ_i represent the rate constant [illegible]. the transfer of lead from organ i to the blood.

λ^1_i represent the rate constant for the transfer of lead from the blood to organ i.

$\lambda^1{}_u$, $\lambda^1{}_f$ represent respectively, the rate constant for the transfer of lead from the blood to the urine and feces.

R_{fd} represent the rate input of lead to the body from food and water.

$R^1{}_{fd}$, $R^1{}_{air}$ represent the rate input of lead to the blood from food and air, respectively.

BR represent breathing rate.

CA represent concentration of lead in air.

X_A represent the fraction of lead from air absorbed into the blood.

IR_n represent the ingestion rate of food type n.

CE_n represent the concentration of lead in food type n.

X_n represent the fraction of lead absorbed into the blood from food type n.

Relative to a given input and the rate constants λ_i, and $\lambda^1{}_i$, the model will yield the concentration of lead in the various organs at any given time.

In matrix form the above system of equations can be written as

$$\frac{dX}{dt} = AX + B \tag{12}$$

Where: X is the vector of concentration in organs.
A a square matrix of rate constants
B a vector of input rates

If matrix A is known, then the analytical solution to equation (12) is found in any book on differential equations (6). The solution is a sum of exponentials of the form:

$$X = \sum_J C_J Z_J e^{K_J \cdot t} - A^{-1}B$$

Where: J is the dimension of the vector X.
K an eigen value of matrix A
Z the corresponding eigen vector
C a constant depending on initial conditions

Other methods of solution for the system are available through the use of numerical integration routines readily available on computors.

An experiment on rats was devised to be used in conjunction with the model described by Equations (1) to (11). The purpose of the experiment is twofold:

1. to validate the model or suggest modifications.
2. to determine the rate constants of the model, in this case for rats.

Dr. R. M. Forbes, of the Animal Science Laboratory, designed and implemented the experiment with his assistants. In brief, the experiment consisted of 240 adult male albino rats. These rats were divided into six groups, where each group was fed for a total of eight weeks a given level of lead. The levels chosen were 0, 20, 40, 80, 160, and 320 ppm lead. Rats on each level were killed at 0, 1, 2, 4, 8 weeks interval. The remaining rats were all fed for a total of eight additional weeks on the 0 lead basol, with some being killed at similar time intervals. Tissues were prepared for analysis by wet ashing, dry ashing for bones. Lead determination was made by either atomic absorption or anodic stripping voltametry (7). For the purposes of the model, six organs were examined for lead concentration at the time intervals specified above; the organs are: Bone, Liver, Muscle, Kidney, Spleen, and Blood.

All the data have been collected as of this date, but the analysis required to determine the role constants and validate the model is not yet completed, and, therefore, no final conclusion can be reached at this stage. Nevertheless, during the data collection, some experimentation on the model was made. The approach taken was to assume certain values for the rate constants (i.e. λ and λ^1), compile the predicted concentrations, and compare them with the reported concentrations; then readjust the rate constants and repeat the process, until the predicted values were matching, satisfactorily, the measured concentrations that were available. This process of calibration was accomplished using CSMP on an IBM 360/75 of the University of Illinois. The final tuning of the model, using this trial and error method, was stopped when the complete data were available. Regression analysis is being used now.

Figure 3 to Figure 8 show the results of the initial effort for a level of input of 360 ppm lead. The actual concentrations of lead over time is plotted for all organs, together with the concentrations calculated from the model. All that can be said at this stage, is that the preliminary results from the model look very promising.

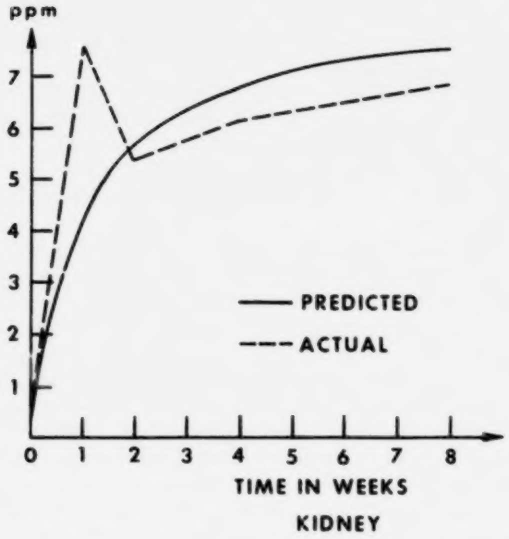


Figure 3. Predicted and actual concentration of lead.

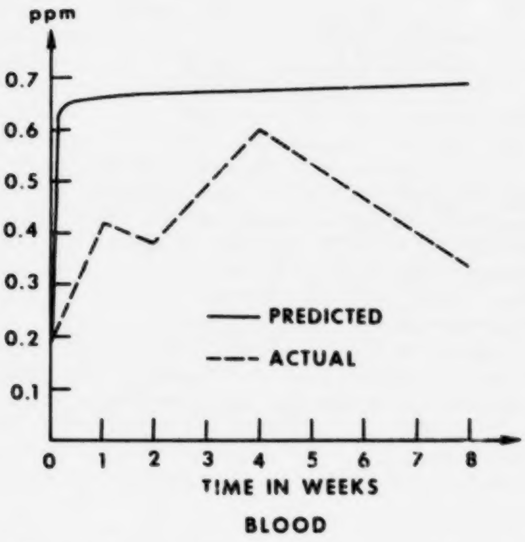


Figure 4. Predicted and actual concentration of lead.

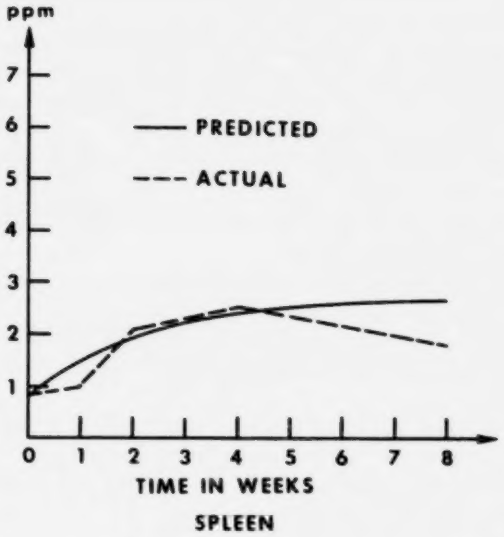


Figure 5. Predicted and actual concentration of lead.

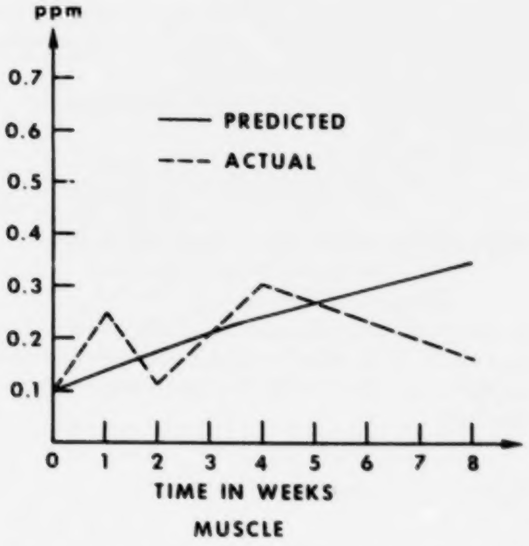


Figure 6. Predicted and actual concentration of lead.

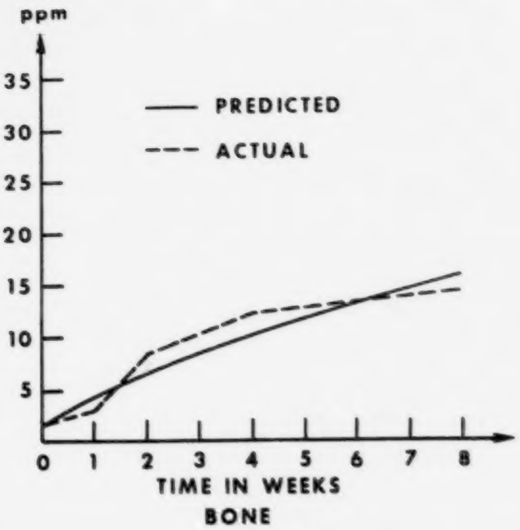


Figure 7. Predicted and actual concentration of lead.

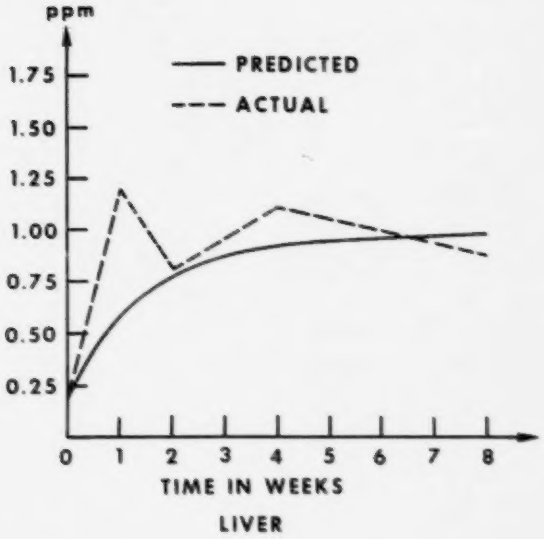


Figure 8. Predicted and actual concentration of lead.

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PANEL DISCUSSION
EFFECTS AND ESTABLISHMENT OF CRITERIA

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EFFECTS AND DEVELOPMENT OF CRITERIA AND THE ESTABLISHMENT OF STANDARDS

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We are primarily concerned with the effects on man. The effects on man's welfare, such as the effects on vegetation, the quality of his waters, beaches, parks, or quality of the paint finish on his car or home, are of secondary importance. The people who study effects try to get quantitative information, as best as possible, on the level of the pollutant and the effect caused by that level; this is an extremely difficult thing to do. A lot of information, look at the upper end of the curve if you were to plot effects versus level, might be obtained from mortality statistical tables, or from occupational health tables. Perhaps a lot of information could be obtained from studies with large overdoses, or even moderate doses, using animals in the laboratory or other types of organisms. Lesser amounts of data are obtained by studying the effects caused by low doses over longer periods of time. For example: The effects of atmospheric pollution due to smoking may not come up for twenty, thirty, or forty years, if at all. Yet we know that there are some people who may be affected within a few years, and once the damage is done it is extremely critical. The experimenters who look at these subtle effects really don't have much time. If we look at genetic effects, there certainly is not much time. It's hard to accelerate studies like this. We use animals that have smaller life cycles and continue studies of that sort. On man himself, we have to try to postulate what will happen. We get data from children who are sick, and as in other organisms, the young are more susceptible to damage by pollutants than the adults. The experimenters or researchers "home in" on such numbers as parts per million or per billion. Many of these experiments are being conducted by epidemiologists where there is a great deal of statistics involved. When orders of magnitude are closely studied, the threshold (not a threshold) can be selected for protecting man. We are talking about parts per billion over a range of six orders of magnitude, say from one part in a thousand to a part per billion, and if when we are able to "home in" within a factor of two or three, I think we're doing an excellent job. When we look at these numbers within the agency, we try to pick a good trade-off. Now let me back off a minute. When I say a trade-off I do not mean a compromise. I mean a practical trade-off. For example, are we to protect every single individual? If the data come from statistics, we really can't. We really have no feel for that. On the other hand, if we know that it is very economic to have a standard set at a certain level, because that level is approximately where the polluters are operating, and this is what man can tolerate, we have a high degree of confidence that our numbers are right, even though there are low-level effects and some effects the level of which we're not quite sure. If you look at that, that is an easy way out. Then you might say that, 10 percent or five percent or one percent or even one part in a thousand of our population is really going to be affected, especially the young. We do try to protect as much as possible of the population, however, most levels might be where you're protecting 99.99 percent of the population if possible. It's true that we do exist in this environment. It is also true that we don't want to give up our standard of living or the way we live. For example, the automobile. None of us is willing to give up the automobile because of lead pollution, even though about 50,000 people a year lose their lives in accidents. We're not willing to make that trade-off. So these are the things to consider. Now the people who set the standards start off with what we call a criteria document, which is a document put together to represent the total important knowledge on that subject. When I say important, I mean that the people who have put these documents together are usually large groups of people. EPA sometimes does it in-house. We do it with the National Academy of Science; we'll use other organizations. We'll use a lot of other consultants. What really comes out of it is really an academic tone, so to speak; almost a handbook or encyclopedia of that particular pollutant, listing what its sources are, what its transport mechanism is, its chemistry, its physics, how it affects man, how if affects the environment, how it is measured, perhaps how it may be controlled, or do we have a control? If we know that something is extremely harmful we still may not be able to measure it because such a small amount hurts us. We may not be able to control it. It may be beyond the technology, yet we know we do have to protect ourselves; and this document is what we call a criteria document. It has all the information in it, as best we know, which has come from all the knowledgeable people and knowledgeable sources. When I say total important knowledge, I mean that we have certainly distilled what is in the literature. We cannot of course afford to, nor are we interested in, even though we do read every word or we think the people who put these together read every piece of literature, but they certainly do not combine all of it. They really digest and use the important ones. And they do come up with recommendations. Finally, looking at it from many viewpoints, from the viewpoint of the person who wants to protect the last man, as to how low a standard should be, to one who is very practical, who is interested in what the economic cost or risk benefit trade-offs might be, or as is stated in the new water legislation, to use the best practical means and later on the best technological available means perhaps regardless of cost within reason, of course, and this is how our standards are set. Let me make a comment about that. I think we could almost get rid of a great deal of our pollution. For example, this is not too far-fetched, it is not economic to use plasma arc and essentially ionize everything we have. Of course we will still come out with the basic elements, but we will have gotten rid of the pollutants in many undesirable forms like pesticides, or bacteria, or other toxic substances. There are ways of doing it; of course, we cannot afford that. We do try to put together standards on a rational basis from many viewpoints, and when the various people, or people who have interests in these things, come together, by the way these documents are standards before they are set, even are promulgated, the agency as well as other agencies or other things do hold hearings and all the information is put together. Finally, it is the responsibility of the administrator of the EPA to set a standard and then it becomes law. One of the things I forgot to mention is that knowing the sources of a given pollutant, we then have to decide how we ration this. If you want to keep the ambient air down, and we know all the sources in a given region, we have to ration that amount of that type of pollutant among all the sources. That is a tough decision. With regard to what a man might take in; we don't just look at what comes in through the water or through the air, but also what is he taking in through the food. How much normally exists in his body? How much does his body retain, and how much does his body take out? Just because a pollutant level is extremely high in the body doesn't mean that it has an effect on it. Maybe it has no effect, and we really try to look at the effects. Then make these trade-offs and then finally come up with these standards.

EFFECTS AND ESTABLISHMENT OF CRITERIA

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Time does not permit a detailed discussion of the effects of the various parameters, or an enumeration of numbers recommended as criteria. I should prefer to discuss and quote the general rationale involved in the establishment of criteria for sources of water for public water supplies, because it is important to understand how the numbers were derived.

CRITERIA

The establishment of criteria represents an attempt to quantify water quality in terms of its physical, chemical, biological and aesthetic values. The problem of establishing criteria lies with the availability of objective and subjective data.

To the extent that scientific data are available, the evaluations for the derivation of recommendations may be overly restrictive and pose an unnecessary economic burden, or they may provide only a limited protection from the hazards that they are intended to prevent. If adequate criteria for recommendations are available, and the analytical identifications and monitoring procedures are sound, the fundamentals are then available to establish effective standards. At this step, political, social, and economic factors enter into the decision.

QUALITY CRITERIA FOR PUBLIC WATER SUPPLY SOURCES

Modern water management techniques and a wide variety of available water treatment processes make possible the use of raw water of almost any quality to produce an acceptable public water supply. For this reason it is both possible and desirable to consider water management alternatives and treatment procedures in making recommendations on the quality of raw water to be used for public supply. Furthermore, these recommendations must be consistent with the effort and money it is reasonable to expect an individual, company, or municipality to expend to produce a potable water supply. Defining a reasonable effort, including the treatment process, involves consideration of the present quality of water, the degree of improvement in raw water that is attainable within the bounds of natural and man-made controls on water quality. Therefore, in evaluating the basis for the recommendations that follow, the Panel left water management alternatives open wherever possible, but it did make certain arbitrary assumptions about the treatment process.

THE DEFINED TREATMENT PROCESS

Surface water supplies characteristically contain suspended sediment in varying amounts and are subject to bacterial and viral contamination. Therefore, it was assumed that the following defined treatment, and no more, would be given raw surface water by a qualified operator prior to human consumption:

1. coagulation (less than about 50 milligrams per liter (mg/1) alum, ferric sulfate, or copperas with alkali or acid addition as necessary, but without coagulant aids or activated carbon);
2. sedimentation (six hours or less);
3. rapid sand filtration (three gallons per square foot per minute or more);
4. disinfection with chlorine (without consideration to concentration or form of chlorine residual).

The panel recognized that, on one hand, some raw surface waters will meet current Federal Drinking Water Standards with no treatment other than disinfection, and that, on the other hand, almost any water, including sea water and grossly polluted fresh water, can be made potable for a price, by treatment processes already developed. However, the defined treatment outlined above is considered reasonable in view of both the generally attainable quality of raw surface waters, and the protection made imperative by the current practice of using streams to transport and degrade wastes. Assumption of the defined treatment process throughout this report is not meant to deny the availability, need, or practicality of other water treatment processes.

Unlike surface waters, ground waters characteristically contain little or no suspended sediment, and are largely free and easily protected from bacterial and viral contamination. See Ground Water Characteristics below for significant exceptions. Therefore, no defined treatment is assumed for raw ground water designated for use as a public supply, although this does not deny the availability, need, or practicality of treatment. Ground waters should meet current Federal Drinking Water Standards in regard to bacteriological characteristics and content of toxic substances, thus permitting an acceptable public water supply to be produced with no treatment, providing natural water quality is adequate in other respects. Unless specified otherwise, the water quality recommendations apply to both surface water and ground water sources.

WATER QUALITY RECOMMENDATIONS

The Panel has defined water quality recommendations as those limits of characteristics and concentrations of substances in raw waters that will allow the production of a safe, clear, potable, aesthetically pleasing and acceptable public water supply after treatment. In setting these recommendations, the Panel recognized that most of the surface water treatment plants, providing water for domestic use in the United States, are relatively small. They do not have sophisticated technical controls, and are operated by individuals whose training in modern methods varies widely in extent.

The recommendations of the public water supply panel should not be construed as latitude to add substances to waters where the existing quality is superior to that called for in the recommendations. Degradation of raw water sources of quality higher than that specified should be minimized in order to preserve operational safety factors and economics of treatment.

The Panel considered factors of safety for each of the toxic substances discussed, but numerical factors of safety were employed only where data are available on the known no-effect level or the minimum effect level of the substances on humans. These factors were selected on the basis of the degree of hazard and the fraction of daily intake, of each substance, that can reasonably be assigned to water.

The recommendations should be regarded as guides in the control of health hazards, and not as fine lines between safe and dangerous concentrations. The amount and length of time, by which figures in the recommendations may be exceeded without injury to health, depends upon the nature of the contaminant, whether high concentrations, even for short periods, produce acute poisoning, whether the effects are cumulative, how frequently high concentrations occur, and how long they last. All these factors must be considered in deciding whether a hazardous situation exists.

Although some of the toxic substances considered are known to be associated with suspended solids, in raw surface waters, which might be removed, to some extent, by the defined treatment process, the degree of removal of the various soluble toxic substances is not generally known; and even if known, it could not be assured under present treatment practices. Therefore, in the interest of safety, it was usually assumed that there is no removal of toxic substances as a result of the defined treatment process.

Substances not included in the report are not necessarily innocuous in public water supply sources. It would be impractical to prepare a compendium of all toxic, deleterious, or otherwise unwelcomed agents, both organic and inorganic, that may enter a surface water supply. In specific locations it may become necessary to determine the presence of substances not considered in the report, particularly where local pollution indicates that the substance may have a significant effect on the beneficial use of water for public supplies.

In summary: the recommendations in the report for raw water quality for public supplies assure that the water will be potable, for surface water, with the defined treatment process; for ground water, with no treatment whatsoever. For waters zoned for public supply, but not meeting the recommendations in all respects, the recommendations can be considered a minimum target toward which efforts at upgrading the quality should be directed. In some instances, the natural quality of raw water may make meeting certain recommendations impractical, or even impossible. For constituents for which this is the case, and where health is not a factor, the natural quality of the water can be considered a reasonable target toward which to work, although determination of natural quality may require considerable effort, expense, and time. Wherever water quality is found superior to that described in the recommendations, efforts should be made to minimize its degradation.

GROUND WATER CHARACTERISTICS

Development of water quality recommendations for ground water bodies must provide for the significant differences between surface water and ground water. Ground water is generally not confined in a discrete channel. Its quality can be measured, in any detail, with difficulty and at great expense. A thorough knowledge of the hydrologic characteristics of the ground water body may be obtained after extensive study. Movement of ground water can be extremely slow; so that pollution occurring today in one part of an aquifer may not become evident at a point of withdrawal for several, tens, hundreds, or even thousands of years.

Wastes mix differently with ground waters than they do with surface waters. Where allowance for a mixing zone, in the immediate vicinity of a waste outfall, can be provided for in surface water standards, under the assumption that mixing is complete within a short distance downstream, dispersion of waste, in a ground water body, may not be complete for many years. The long retention time will facilitate bacterial or chemical reactions with aquifer components that result in removal or decomposition of a pollutant to the point where it no longer degrades the aquifer. Because these reactions are imperfectly known and cannot be predicted at the present time, it is necessary to monitor the movement of waste in a ground water body from the point of introduction outward. Unlike bodies of surface water, bodies of ground water cannot be monitored adequately by sampling at the point of use.

Inadvertent or careless contamination of fresh ground water bodies is occurring today from the leaching of accumulated salts from irrigation, animal feed lots, road salt, agricultural fertilizers, and dumps and landfills; or from leakage of sewerlines in sandy soil, septic tank effluents, petroleum product pipelines, and chemical waste lagoons. Another source of contamination is the upward movement of saline water in improperly plugged wells and drill holes, or as the result of excessive withdrawal of ground water. Deep-well injection causes intentional introduction of wastes into saline ground water bodies.

Because of their common use as private water supplies in rural areas, all geologically unconfined, water-table, aquifers could be placed in a classification comparable to that for raw surface waters used for public water supplies. Even though not all waters in these aquifers are suitable for use without treatment, such classification could be used to prohibit introduction of wastes into them. This would restrict the use of landfills and other surface disposal practices. Limited use of the unsaturated zone for disposal of wastes would still be acceptable, provided that decomposition of organic wastes and sorption of pollutants, in the zone of aeration, were essentially complete before the drain water reached the water table. Bodies of artesian ground water, in present use as public and private supplies, could be similarly classified wherever their natural source of recharge was sufficient to sustain the current yield and quality.

Disposal of wastes, in either of the above types of aquifers, could be expressly forbidden on the basis of their classification as public water supplies. Furthermore, before disposal of wastes to the soil or bedrock adjacent to aquifers used or usable for public supply were permitted, it could be required that a geologic reconnaissance be made to determine possible effects on ground water quality.

Water quality recommendations, for raw ground waters to be used for public water supplies, are more restrictive than water quality recommendations, for raw surface water sources, because of the assumption that no treatment will be given to the ground waters. The distinction between surface and ground waters is, therefore, necessary for proper application of the recommendations. In certain cases, this distinction is not easily made. For example, collector wells in shallow river valley alluvium, wells tapping cavernous limestone, and certain other types of shallow wells may intercept water only a short distance away, or after only a brief period of travel, from the point at which it was surface water. Springs used as raw water sources present a similar problem. Choice of the appropriate water quality recommendations, to apply to such raw water sources, should be based on the individual situation.

WATER MANAGEMENT CONSIDERATIONS

The purpose of establishing water quality recommendations and, subsequently, establishing water quality standards is to protect the nation's water from degradation, and provide a basis for improvement of their quality. These actions should not preclude the use of good water management practices. For example, it may be possible to supplement streamflow with ground water pumped from wells, or to replace ground water removed from an aquifer with surface water through artificial recharge. These other sources of water may be of lower quality than the water originally present, but it should remain a management choice whether this lower quality is preferable to no water at all. In arid parts of the nation, water management practices of this sort have been applied for many years to partially offset the effects of mining of ground water. Example, its withdrawal at a faster rate than it can be recharged naturally.

It is possible, by merely removing ground water from the aquifer, to degrade the quality of that remaining, by inducing recharge from a surface or ground water body of lesser quality. It does not seem reasonable to forbid the use of the high-quality water that is there because of this potential degradation. Of what value is it if it cannot be used?

It would appear, that degradation by choice might be an alternative under certain conditions and within certain limits. This type of degradation is not comparable to that resulting from disposal of wastes in the water body. It is simply the price exacted for using the water. In the case of mining without artificial recharge, the philosophy involved is the same as that applied to the mining of other nonrenewable resources such as metal ores or fossil fuels. Because considerations of recreation and aesthetics, and the maintenance of fish and wildlife are generally not involved in this kind of management situation, it is reasonable that water quality standards should provide for the mining and artificial recharge of bodies of ground water zoned for public supply. As in any water management program, it would be necessary to understand the hydrologic system and to monitor changes induced in the system by management activities.

Preservation of water management choices can be protected by water use classification. Classification of surface waters has not been based solely on the fact that those waters are being used for public supply at the present time. Presumably, it has been based on the decision that the body of water in question should be usable for public supply with no more than the routine forms of water treatment, whether or not it is presently in use for that purpose. Conversely, failure to zone a body of water for public supply would not necessarily preclude its use for that purpose. Selective zoning could thus be used to assure desirable water management.

HUMAN STUDIES LABORATORY

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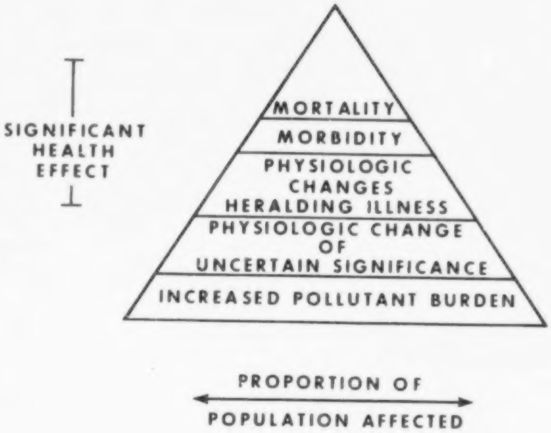
Within the U.S. Environmental Protection Agency, the Human Studies Laboratory (HSL) has been given primary responsibility for developing the health intelligence necessary for the establishment of adequate environmental quality standards. This task is complicated by the fact that little information is available concerning the following topics:

1. What are the toxic materials now present in the environment?
2. What is the potential for newly developed materials being toxic, particularly as a result of long-term exposure to low levels?
3. If a screening procedure suggests a high toxicity potential for particular materials, how do we determine levels of environmental exposure? (This may not be HSL's responsibility, but the knowledge is vital if any kind of priorities for studies are to be established.)
4. What is the significance of the various formulations of a toxic substance, example, how do the physical and chemical properties of the various compounds relate to its toxicity?

Assuming that estimates of these factors can be developed, additional concern must be given to measurements of total intake and routes of intake as well as to absorption, distribution, storage and excretion of the individual material.

Finally, the Human Studies Laboratory must be concerned with the entire biologic spectrum of response that may occur as a result of exposure. This is illustrated by the following figure.


SIGNIFICANT HEALTH EFFECT
MORTALITY
MORBIDITY
PHYSIOLOGIC CHANGES HERALDING ILLNESS
PHYSIOLOGIC CHANGE OF UNCERTAIN SIGNIFICANCE
INCREASED POLLUTANT BURDEN
PROPORTION OF POPULATION AFFECTED

Responding to these needs is the goal of the EPA, Human Studies Program. Obviously, there are many difficulties and many problems not yet solved. At present we are forced to rely heavily on occupational data that for several reasons are less than satisfactory.

However, since the need and the obligation to protect human health surmounts all other responsibilities, we utilize the best data available to develop recommendations when they are needed, and recommendations for whatever action appears to be necessary to assure adequate protection for even the more susceptible or sensitive segments of our population.

SIGNIFICANT EFFECT OF POLLUTANTS

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One of the problems with which we must wrestle in the environmental field, and especially in the area of criteria establishment, is to determine what is a significant effect of a given pollutant. If we can provide definition of a significant effect, then the overall problem is reduced to monitoring and analysis. I don't mean to minimize the difficulties inherent in these areas but, we may bring our technical expertise to bear on these. Determination of what constitutes a significant effect involves philosophy and judgment. Our technical skills won't do us much good in these areas.

What is a significant effect? This is a question of much controversy. Some would have us believe that a significant effect is any measurable change in man or the environment, while others hold that an effect is not significant unless it produces frank illness in man or measurable harm to the environment. It seems clear that the effects on which criteria are established, and upon which standards are eventually set, must be somewhere in between these two extremes. Admittedly, the ground in between is sometimes extremely broad, and it takes wisdom and courage to define criteria and to set standards in this very grey area; yet this is what must be done. It takes wisdom to decide what constitutes evidence of a significant effect. It takes courage to withstand the pressures of those who want no-risk criteria and standards, and those who would have us reject even minimal safety factors.

Those who advocate the no-risk concept often use the argument that any substance must be shown to have no ill effects before it may be introduced into our environment, and environmental contaminants, about which such information is not available, which are already present must be eliminated or banned. I reject this concept because one can never prove the negative; therefore, it is impractical. Further, widespread acceptance of this concept would cripple our economy and stifle new developments. Unfortunately, there is a disturbing tendency toward this point of view, and some of the recent stringent regulatory action are a result of this philosophy. I cite the recent requirements, of the Clean Air Act, for a 90 percent reduction over 1970 levels of NO_x, CO and unburned hydrocarbons in automobile exhaust, and the talk about zero discharge in the new water pollution act. It is doubtful that there is scientific justification to support those, and other extremely stringent standards; the costs are absolutely awesom.

If we reject the no-risk concept, we must create guidelines for acceptable safety factors. This is no easy matter, but I think before we base a criteria on an effect, we must ask at least two questions:

1. Is the effect in question a detrimental one? Some effects which are attributed to environmental stresses can be classed as compensatory responses, but may be of no known detriment to health. The inhibitory effect of lead on erythrocytic-ALA dehydrase may be an example of this type of an effect.
2. What are the trade-offs? The safest approach is to use the most sensitive effect as a criterion. However, we must take into consideration the economic costs of controlling to very stringent low levles. We must also be concerned about potential substitutes which may result in environmental problems of even greater magnitude. An example here is the elimination of lead from gasoline, wherein, the costs may be exorbitant in terms of higher gasoline prices, lowered fuel economy, depletion of petroleum reserves, and the possible increase of aromatic hydrocarbons into the air.

I recommend that we base criteria on known harmful effects, and establish our safety factors with full knowledge and consideration of the economic and environmental disruption which we may cause by over-zealous action.

In the field of trace metals, and with other environmental contaminants, it is extremely important that environmental effects research, both under industrial and governmental sponsorship, continue. Providing both governmental and industrial funding assures a balanced interpretation of data. Further action on pollutants must then be taken, based on these data, and the answer to the two questions: Is the effect

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harmful? Will it do more harm than good to replace or eliminate the pollutant?

If scientists address themselves to these questions and provide answers and interpretation, then we may see a more deliberate approach to criteria establishment and standard selling, but an approach which at the same time, will protect our society and our environment with a minimum disruption to our economic well being.

STATEMENT ON ESTABLISHMENT OF CRITERIA FOR METALS IN FOODS

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Washington, D. C.

In the Bureau of Foods program, to assess the hazards of toxic elements in foods, we must be governed by the fact that man experiences a finite level of intake of all the elements in the earth's crust, as demonstrated by their presence in the human tissue (1). We are dealing with materials that enter food through natural geologic causes as well as man's activity. Our problem is to determine what level of exposure, from food, is consistent with safety. In the process of determining an acceptable level of exposure to a metal from any given food, it is essential to define the level of unavoidable background exposure from all environmental sources, such as food, water and air. This is in marked contrast to criteria usually employed with a new substance proposed for addition to food or water, where sources of exposure can be better controlled.

In our approach to this problem, we feel we must, determine the overall level of occurrence of the toxic elements in food in order to obtain a good indication of the natural background level in food, and find out whether specific components of the food supply contain unusually high levels, so that potential problems are readily identified. In determining levels of exposure compatible with health, we must take into account all sources and routes of exposure. For example, although mercury exposure is almost entirely through the diet, significant exposure to lead can occur from air, water, industrial exposure and pica.

In regards to occurrence of a given metal in our food supply, we must not only obtain data on the general level in the total food supply, but also develop information on the frequency distribution in the various food classes of the diet and on food consumption patterns. Our establishment of mercury guidelines of 0.5 ppm in fish was simplified by the fact that they could be based on methyl mercury toxicity, and on information concerning fish consumption, since no other significant environmental exposures occur. For lead, cadmium, and other elements that may be ubiquitous in the food supply, the problem of setting acceptable intakes becomes much more complex. We must not only carry out surveys of such metals in the principal dietary items, but must also take into account that consumption patterns differ with age. For example, the diet of very young infants is almost exclusively milk.

We must consider the chemical form and bioavailability of the metal concerned. Well known effects along these lines are the increased toxicity and bioavailability of methyl mercury, and that the form in which arsenic exists in shrimp is essentially physiologically inactive.

I would now like to bring you up to date on our surveillance activities on toxic metals in the food supply. Our general philosophy is to develop a full picture of the occurrence of the metals of interest in food before setting guidelines, unless a hot spot occurs, in which case a specific guideline will be set for this particular situation, based on the best information at hand concerning exposure, bioavailability and toxicity.

For example, when it became obvious to us that dangerous amounts of lead and cadmium could be leached from ceramic ware, because of improper firing, we established interim guidelines for leachable amounts of these metals, and have continued carrying out an active monitoring program on these items, especially of imports, which have been the bad actors.

In determining the overall level of occurrence, of a contaminant in the food supply, we conduct continuing surveys on the Total Diet, which is based on consumption data, developed by the USDA, seven years ago. We analyze composite samples of 12 different food classes, and calculate the intake of a given metal based on the average total consumption of a young male adult, which is appreciably more than that of the average adult. The latest information published covers the levels of arsenic and cadmium in the Total Diet from June, 1968 to April, 1970 (2). The average overall level for both of these metals in the Total Diet was around 0.02 ppm, which we do not regard as hazardous. Mercury was added to the Total Diet Survey in June, 1970, and selenium, lead, and zinc were added in June of this year.

We also carry out a special Fish Survey to determine the levels of contamination in a variety of sea and fresh water fish. This fiscal year we have mercury, lead, and cadmium in our Fish Survey, and plan to add at least selenium, arsenic, and zinc next fiscal year.

We also carry out Surveys in a variety of food types to obtain a clearer idea of the levels in important foods. I mentioned to you that the setting of a guideline for mercury in food was simplified by the fact that it occurs, in significant amounts, only in fish. Nevertheless, we continued monitoring different food categories for mercury to make sure that the situation had not changed. Perhaps you have seen the recent article in Science (3), where we reported that the median concentrations of mercury in a variety of foods varied from less than 0.001 ppm to 0.014 ppm; all well below the 0.5 ppm guideline. This year we are carrying out a similar survey, on cadmium, in a variety of foods.

In carrying out these surveys, we must be sure we use reliable analytical methods having satisfactory sensitivity, accuracy and reproducibility. Dr. Haenni, of the Bureau of Foods, will go into this subject in more depth tomorrow.

In addition to developing information on the levels of toxic metals in foods, as described above, we naturally consider the toxicological properties of the metals. There has been a great deal of information published on this subject, which we take into consideration. In addition, we are conducting active toxicological evaluations of mercury, lead, and cadmium ourselves.

We are devoting considerable analytical, toxicological, and inspectional manpower to obtain accurate information on overall occurrence of the toxic elements in foods, and, at the same time, maintain an alert for special trouble spots which may arise. Our overall ambitions are not small. We plan to move progressively, from the six metals we are now evaluating to those which we feel pose less hazard, until we have assessed about 20 in all.

This is a much bigger program than we can push through all at once. Our objective has been to use our resources to concentrate on the most potentially hazardous metals first; systematically develop necessary data for guidelines, but at the same time maintain flexibility to our approach to be able to provide protection to the consumer when a real problem arises.

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BIOMEDICAL RESEARCH IN SUPPORT OF CRITERIA AND STANDARDS

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The development of an environmental standard rests on the basic assumption that some kind of a dose-response relationship can be developed for the environmental agent in question; that a curve can be envisaged on a graph relating degree of exposure, quantitatively expressed on the horizontal axis, to probable effect, quantitatively expressed on the vertical axis. It is the business of criteria, supporting the standard, to develop and justify the relationship to be so expressed.

The assumption is perfectly valid in a conceptual sense, but considerable difficulties are often experienced when one tries to apply it to a particular agent. Many intervening factors determine how much of a particular agent, whose concentration in the surrounding air, in drinking water, or in food is known, actually enters into the body of the exposed person to constitute the actual dose. Previous speakers have dealt with some of these determinants, and it is clear that the regulatory agencies and the technical experts, that they command, have gotten fairly close to methods of predicting what persons, exposed to a particular situation, will probably receive. Our ability to enter the horizontal axis of the hypothetical dose-response chart is in reasonably good shape and rapidly improving.

Unfortunately, we are not in nearly such good shape with regard to the vertical or response axis. It is not always clear even what should be used as the response. Easily measured reactions, such as the pulse rate, may be unaffected, or so influenced by extraneous factors, as to be unreliable. Sick absences have some built-in uncertainties. Subjective complaints like headache or loss of appetite are very hard to quantify. No one wants to wait for a specific disease to provide a measurable effect.

Even if we agree upon the response to be used, it is very clear that people are far from being equal. A highly susceptible person may react violently to a dose that passes unnoticed by the average person. Children often respond more or less readily than their elders. Sex, race, the physiological state at the moment, co-existent disease, self-medication, and a host of conditions create a spectrum of human variability that can be broken down into arbitrary segments only with some risk of injustice to the borderline instances. Furthermore, one can look only indirectly at what goes on in the human body, and often has to rely on animal experiments which introduce their own problems.

Our luncheon speaker, Dr. Laitinen, mentioned some areas of uncertainty about the way in which metallic substances produce adverse effects and about the determinants of biomedical action. Had he had more time I am sure that his list would have been much longer. If you will stand with me outside of the system for a moment, and try to follow a metallic molecule in its bodily perigrinations, I think you will see what I mean. If, on coming from the outside, the molecule enters the lung, it may simply be breathed out again, stick on the wall of the large airways, pass through into the blood stream, or be passed for some time from one macrophage cell to another. Its fate depends upon its size, attachment to a larger particle, immediate toxicity for a cell, or just pure chance. Some of the probabilities are known, but only some, and these fairly grossly. If it enters the alimentary canal, its chances of absorption will vary with its valency, its aggregation, the presence of materials with which it can combine and be removed from the scene, the health of the alimentary wall, intestinal motility, etc., etc.

In the bloodstream, after absorption, it may be carried in solution, be bound with lipid or protein, or enter a red blood cell. This disposition, in turn, will affect the ease with which it can pass from the blood to intercellular fluid and then to tissue cells. Whether it can pass into the cell will depend upon the state of the cell membrane, the presence of carriers, and what the metal itself does to the cell membrane constituents. As pointed out by Dr. Abdelnour, the concentration in the blood is both the result of past exchanges with cells and the determinant of future exchanges; a very complex set of balances. Within the cell, the metallic material may undergo various changes of state; some decreasing its chance of adverse effects; some enhancing it. Storage and release from storage in such material as bone, often treated as a simple, reversible, linear process, is in reality a very complex set of balances and interactions, subject to much variation.

Those molecules that, as a result of all the foregoing balances and exchanges, manage to impinge on a reactive cell site may produce quite critical events. They may combine with sulfhydryl groups and change the permeability, if not, the structure of membranes. They may enter into and distort enzymic molecules so that they can no longer bring normal reactants together. Or they may provide just the metallic atoms that the enzyme needs for its structure, in which case we would call them essential metals. They may change the solubility of some reactants, removing them from desirable processes. The more one presses the question, Just why is this metal toxic?, the more uncertain the answers tend to become. Finally, the process of excretion involves a triple problem of uncertainty. The cells of excretory organs are vulnerable just as other cells; they exercise a special metabolic relationship with the material being excreted, and they are often exposed to much higher concentrations of the material than are other cells.

In the face of all this uncertainty, what is the standard-setter to do? He clearly cannot sit on his hands until the research boys make up their minds. If there is strong presumptive evidence that an agent is harmful he must set some kind of limit which will protect most, if not all, of those who may be exposed to it. He can only make the best judgment that he can on the basis of the evidence that he has. He, and the public he serves, must recognize that the ideal is approachable only by stages, with amendments introduced as better information becomes available. After all, we have spent 5000 years getting into this mess; but only 5000 days or so worring about it. It is a bit much to expect research to give good answers in 5000 hours. However, the standard-setter can be certain of one thing; whatever judgment he makes will be attacked, and evidence to the contrary will be adduced by those who find the judgment hard to take. To combat pressures, and to ensure the public of the best protection that is justifiable at the time one can recommend just three things: (a) that the various environmental agents be placed in some kind of rank order as regards importance, severity of effect, number of people exposed, relation to other exposures, feasibility of control, etc. (b) that those making the judgment are permitted to do so according to their conscience; regardless of the pressures and interests of those affected, (c) that every opportunity be given, through resources and conditions of work, to those who are trying to see toxicological responses and mechanisms clearly, so that still better judgments can be made in the future.

SESSION III
CONTROL PROCESSES

Chairman:

C. J. Lyons
Battelle's Columbus Laboratories

TRACE METALS IN EFFLUENTS FROM METALLURGICAL OPERATIONS

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INTRODUCTION

The purpose of this paper is to list the current pollution control techniques associated with metallurgical operations, and to present some examples of data describing the behavior of trace metals in waste streams from smelting operations.

The approaches taken to control pollutants in waste streams in metallurgical operations are shown in the summary listing in Table 1 of pollution factors and the methods of control applied to waste gas and water streams. Two basic, and relatively long-term approaches to waste streams are modification of processes to minimize or eliminate the waste stream, and segregation of waste streams to minimize the volume to be treated, to allow the use of a specific treatment method, and to maximize the effectiveness of the treatment. The modification of processes generally involves the time and cost associated with research, development, and equipment changes, while the segregation of waste streams usually involves alteration of existing plant facilities.

In cases where lowering of concentrations of specific impurities is the intent, dilution of waste water with purer water, or with a different waste water, may achieve conformance with discharge limitations. In the case of waste gas streams, dilution, or dispersion may be achieved by means of tall stacks. The standard methods of separating suspended solids from liquid waste streams and particulates from gas streams are listed in Table 1 and include only traditional devices. The term Inorganics refers to dissolved salts in liquid streams and to particulates and vaporized materials, such as, mercury, in gas streams. The term Organics refers to BOD, oil, etc., in water, and to hydrocarbons and vapors in gas streams.

TABLE 1 METHODS OF CONTROL

Waste volume or nature	Process modification waste stream segregation	
	Water	Air
Concentration	Dilution	Tall stacks
Suspended solids	Settling, coagulation	Long flues
	Wet cyclones	Cyclones
	Filtration	Electrostatic precipitators
	Centrifuges	Wet scrubbers Baghouses
Inorganics	Chemical oxidation	Absorption
	Reduction	Reagent injection
	Neutralization	Fabric coatings
	Evaporation	Wet scrubber
	Ion exchange	Solutions
	Electrochemical methods	
Organics	Biological treatment	After burners
	Skimming	Catalytic reactors
Mists and aerosols	—	Electrostatic precipitators Filters

TRACE METALS IN ELECTROSTATIC PRECIPITATORS

The following example of the behavior of trace metals in gases and dusts is taken from an exercise carried out at a combined copper-zinc smelting plant (1). The point of the exercise was the recovery of metal values in a mixture suitable for use in the existing process equipment. The data obtained have been analyzed to obtain insight into the behavior of the trace metals in the control devices.

A flowsheet, depicting the major features of the metallurgical operation and the dust control equipment

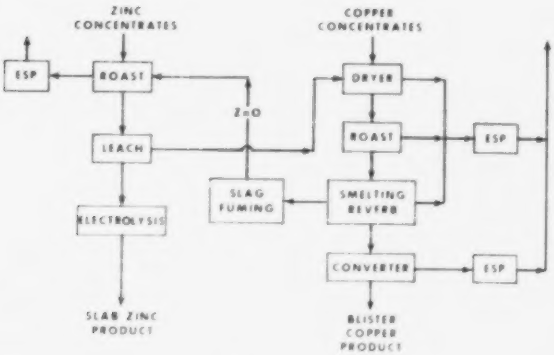

Figure 1. Flowsheet for Cu-Zn smelting plant.

present before a program of alterations, is shown in Figure 1. Zinc and copper flotation concentrates were processed to electrolytic zinc and blister copper products. The two processes were interrelated by the transfer of zinc leach residues to the copper operation, and the transfer of slag-fuming product, ZNO, from the copper reverberatory furnace slags to the zinc operation.

The alterations made in the dust control systems on the copper process during the plant revisions are shown in Figure 2. Initially, the gases from drying kilns, roasters, and reverberatory furnaces were treated in four electrostatic precipitator units in series. Converter gases were treated in a separate precipitator unit. In the altered arrangement, the roaster gases were treated in half of the original precipitator capacity, and the reverberatory gases were treated in the other half of the precipitator capacity. The reverberatory furnace and converter gases flowed from their precipitators to a baghouse for additional dust recovery.

Some of the characteristics of the gas streams and trace metals in the dusts from this smelting operation are presented in Table 2. The dryer dusts represent, to a fair degree, the base composition of the feed to the copper smelting operations. (Major constituents such as SiO_2, Fe, S, etc., are omitted for the sake of brevity.) It may be noted that all of the trace metals are more concentrated, on a percentage basis, in the fume than in the feed material. Cadmium, lead, and arsenic undergo much greater degrees of concentration than do the base metals copper and zinc. The trace metals are concentrated in the fume differently in the various steps of copper smelting.

The collection efficiencies of electrostatic precipitation, for trace metals under the before and after conditions of the plant alteration, are given in Table 3. In the initial condition, a combined stream from dryers, roasters, and reverberatory furnaces was treated with an overall collection efficiency for particulates of 75 percent. Collection efficiencies for the individual metallic elements varied from 40 percent, for cadmium, to 93 percent for antimony. When the roaster gas was segregated to half the original precipitator area, overall collection efficiency for particulates rose to 98.9

TABLE 2 COPPER-ZINC SMELTER WASTE STREAM CHARACTERISTICS

Element	Metals content, weight % of particulates*				
	Dryer dusts	Roaster dusts	Reverb dusts	Converter dusts	Combined flows†
Cu	3.3	9.3	2.7	6.9	2.8
Zn	3.7	8.1	18.4	28.6	27.0
Cd	0.02	1.0	0.6	1.14	0.94
Pb	0.6	1.5	4.9	21.2	14.1
As	0.32	1.05	5.5	2.0	3.09
Sb	0.07	0.27	1.2	0.71	0.27
Ge	—	—	—	—	0.001
Au, oz/ton	0.08	0.11	0.07	0.12	0.06
Ag, oz/ton	3.42	3.03	1.89	100,000	330,000
Flow, scf/m	18,000	67,000	100,000	800	475
Temp., F	325	350	1,020	23	38
Dust burden, tons/day	1	55	48		

*Sulfur, silica, iron, etc., not shown.

†After electrostatic precipitator.

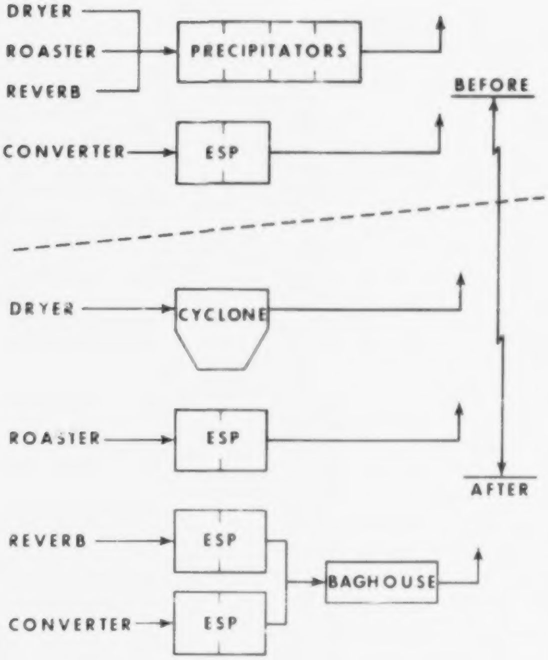

Figure 2. Smelter waste stream routings.

percent. The ratio of flow rate to precipitator area was decreased about 40 percent, and gas temperature decreased about 60 F. The general level of collection of the individual elements increased appropriately except for cadmium and silver, which were improved, but not to the levels of the other elements.

A similar tabulation of the before and after data for the gas stream from the reverberatory furnace, which was segregated and routed through the other half of the precipitator, is presented in Table 4. The ratio of flow rate to precipitator area was about the same as the original condition, and this particular gas stream was about 340 F hotter than the combined streams. A decrease in collection efficiency was observed for total particulates and for most of the individual trace elements. The numbers indicate some small increases in collection efficiency for cadmium and antimony, but these are small and difficult to rationalize in view of the surrounding data.

One other comparison of trace metal collection behavior is afforded from the analyses of the converter dusts. Here, an electrostatic precipitator operating at 800 F showed an overall collection efficiency on total particulates of 26 percent. The collection efficiencies for individual elements is shown in Table 5. In this case, gold, silver, and copper show collection efficiencies above the average for total particulates, while the more

TABLE 3 EFFECT OF CONTROL PRACTICE CHANGES ON SMELTING EFFLUENTS (ROASTER GASES)

Element	Collection efficiencies, %	
	Before	After
	Combined flows (dryer, roaster, reverb)	Roaster gases
Cu	86	99.2
Zn	54	98.4
Cd	40	82.0
Pb	65	96.2
As	56	98.5
Sb	73	99.2
Au	82	98.3
Ag	76	81.4
Flow, scf/m	204,000	600,505
Temp., F	440	380
Dust burden, tons/day, In	95	95
Out	–	0.62
Precipitator area	Ai	Ai/2
Overall efficiency on particulates, %	75	98.9

TABLE 4 EFFECT OF CONTROL PRACTICE CHANGES ON SMELTING EFFLUENTS (REVERB GASES)

Element	Collection efficiencies, %	
	Before	After
	Combined flows (dryer, roaster, reverb)	Reverb gases
Cu	86	75.4
Zn	54	29.0
Cd	40	44.8
Pb	65	48.7
As	56	50.0
Sb	93	99.1
Au	82	57.2
Ag	76	35.4
Flow, scf/m	204,000	97,000
Temp., F	440	780
Dust burden, tons/day, In	95	48
Out	–	18.3
Precipitator area	Ai	Ai/2
Overall efficiency on particulates, %	75	62 (Exit gas to baghouse)

volatile trace metal elements show collection efficiencies in the range of 10 to 15 percent.

TABLE 5 COLLECTION EFFICIENCIES ON CONVERTER GASES AND DUSTS

Element	Collection efficiencies, %
Cu	85
Zn	15
Cd	16
Pb	13
As	11
Sb	10
Au	94
Ag	55
Gas flow, scf/m	100,000
Temp., F	800
Dust burden, tons/day	23
Overall efficiency on particulates, %	26 (Exit gas to baghouse)

The baghouses added to the plant collected dust with metal contents as shown in Table 6. This dust is, of course, the feed material for the zinc leaching operation, with significant values of cadmium and lead.

With the changes described, the plant upgraded precipitator collection performance from 75 percent to 98.9 percent on the roaster gases, and went from precipitator performances of 75 percent and 26 percent on the reverberatory furnace and converter gases to baghouse treatment and associated higher collection efficiencies.

TRACE METALS IN COPPER SMELTING OPERATIONS

As analytical work proceeds, some operations are developing detailed knowledge of the behavior of trace metals in their manufacturing processes. Two examples of the behavior of trace metals in plant operations follow.

The factors in this example are indicated by the partial flow diagram in Figure 3. The operation is typical for the copper industry, consisting of ore flotation concentration, reverberatory furnace smelting, and converting. The control device of interest is the cyclone on the converter. The reported efficiency of this cyclone for collection of total particulates was 85 percent.

The available analytical data on trace metals in this system are shown in Table 7. Some of the trace metals appear in significant quantities only in the latter stages of processing. In the ore, for example, arsenic is less than 1 ppm and selenium is reported as 50 ppm. The reverberatory furnace feed is the product from the flotation concentration process. Analysis of this material shows that trace metals are concentrating with the copper, although zinc is the only metal concentrating at a rate even approaching that of copper. The analyses of interest are those of the dusts from the converter flue, the converter cyclone catch, and the dust issuing from the converter stack. Although the analyses do not allow a rigorous determination of in-out control effectiveness for the cyclone, some observations may be made. The elements arsenic, cadmium, selenium, zinc, and to a slight extent, chromium appear in higher percentages in the stack dust than in the dust captured in the flue or cyclone. Although highly variable in occurrence, selenium appears to be concentrating in the system in terms of both the cyclone catch and the stack loss.

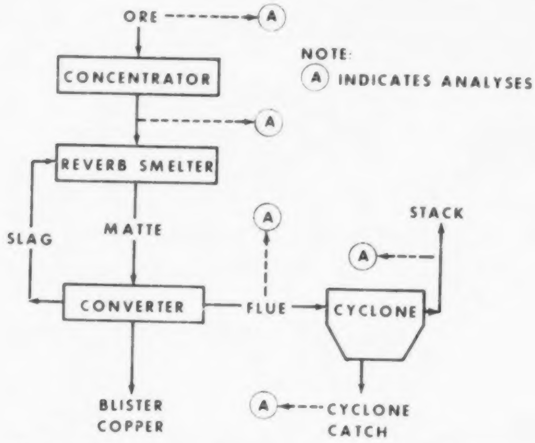

Figure 3. Diagram relating analyses to process steps.

CLEANING SMELTER GASES FOR ACID PLANTS

The recent attention paid to mercury has drawn attention to the trace quantities of mercury found in some nonferrous metal ores. This trace mercury has been identified principally in zinc ores where mercury contents of 20 to 200 ppm are reported. Three zinc smelters, two in the United States and one overseas, have been known to have recovered this trace metal in one way or another. The occasional incidence of mercury in roaster gases has been known for some years to designers of sulfuric acid plants for operation on smelter gases. Lead is a natural choice of materials of construction for gas cleaning trains. The presence of mercury in smelter gases results in corrosive attack of the lead.

TABLE 6 ANALYSES OF BAGHOUSE DUSTS (COMBINED REVERB AND CONVERTER DUSTS AFTER ELECTR ELECTROSTATIC PRECIPITATOR)

Element	Weight %
Cu	1.9
Zn	31
Cd	1.5
Pb	14

Sulfuric acid plants being operated at smelters have established a sequence of gas cleaning steps which remove trace metals and particulates in order to achieve protection of catalysts and saleable grades of acid purity. Estimated upper limits for some trace metal and other constituents in gas streams entering a catalytic sulfuric acid plant have been approximated in Table 8 (2).

A typical gas cleaning train for smelter gases consists of a waste heat boiler, a spray or tower scrubber using weak (30 percent) acid, and always one or more electrostatic precipitators for removal of particulates and demisting (Figure 4). A recently installed overseas facility, for the recovery of mercury from zinc ore roasting gases, had a similar gas cleaning train with the addition between waste heat boiler and weak acid scrubber of a packed tower concentrated acid scrubber (3). In this scrubber, the mercury, and also the selenium, in the gas stream were sulfatized and collected in the acid. The acids from both scrubbers were treated in clarifiers for solid-liquid separation, the liquids returned to the roaster and the solids routed to mercury and selenium recovery operations. Bleeds from the weak-acid scrubber liquor and demisting precipitators required separate treatment by sodium sulfide precipitation to produce solids and a purified acid. It should be noted that this system accounts for zinc and iron being present but makes no mention of cadmium or arsenic. The recovery of mercury is indicated by the data in Table 9.

One of the most common problems, identified in a 1971 survey of smelter waste water problems, was the disposal of the dilute acid which accumulates in the weak-acid scrubbers, spray tower sumps, or precipitator sumps. The liquor is too dilute and too dirty to sell and very difficult to treat. A typical analysis of this liquor is

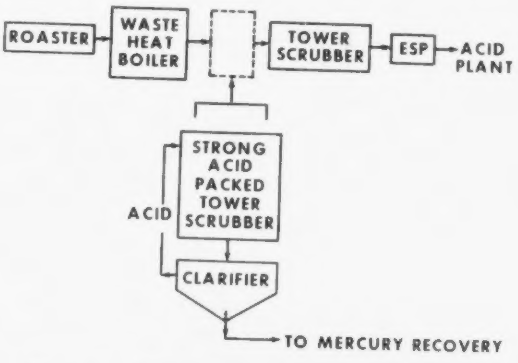

Figure 4. Gas cleaning train for smelter gases.

TABLE 7 TRACE METAL ANALYSES IN A COPPER SMELTING OPERATION

Element	Ore	Reverb feed	Converter flue dust	Converter cyclone catch	Converter cyclone stack
As	<0.0001	0.001	0.003	0.008–0.010	0.003–0.02
Cd			0.0001	0.002	0.001–0.085
Cu	0.9	27.4	25	36–72	2.5–15.0
Se	0.005	0.009	0.0008	0.02–0.32	<0.0001–2.3
Zn	0.013	0.08	0.06	0.06	0.04–4.4
Cr			0.002	0.001	0.003–0.008
Mn			0.005		0.004
Ni	0.006	0.013	0.04	0.036	0.02
V			0.006		0.005

*Cyclone operates at 500 to 600 F.

TABLE 8 ESTIMATED UPPER LIMITES FOR CONSTITUENTS IN GASES ENTERING ACID PLANTS*

Element	Approximate limit grains/standard ft^3
As (as As_2O_3)	0.0005
Pb	0.0005
Hg	0.0001
Se	0.022
Cl	0.0005
F	0.0001

*Reference 2.

TABLE 9 DISTRIBUTION OF MERCURY IN ZINC ORE ROASTING OPERATION *

In concentrate	20–200 ppm
In roaster gas	0.0043–0.0348 grain/scf
Gas after Hg removal	0.000046–0.000092 grain/scf
Hg in H_2SO_4	0.2–0.4 ppm
Hg recovery	99.5%

*Reference 3.

TABLE 10 COMPOSITIONS OF ACID PLANT WATERS, mg/liter

Element	Plant A (neutralized)	Plant B
pH	5.0	1.9
As	–	22.1
Cd	7.7	0.60
Cu	0.06	7.43
Fe	7.4	–
Mn	0.7	–
Ni	0.2	–
Pb	0.5	7.23
Zn	8.0	7.3
SO_4	960	1716
Se	–	0.71

given in Table 10. The Finnish system described above included a sodium sulfide precipitation treatment to clean up the final bleed stream and by returning waste water and gases to the roaster achieved closed loops. No accounting was shown for such constituents as arsenic, cadmium, etc.

Thus, the specific solutions to the problems of disposal of acid plant waters are currently being evolved by industry. It remains to be seen which of the possible alternatives mentioned by industry in the prior survey prove to be most feasible for the various plants. The alternatives mentioned included. precipitation with SO_2, neutralization, evaporation, deep well injection, and undesignated approaches to recovery.

These examples have shown the types and concentrations of trace metals encountered in waste streams from copper and zinc smelting operations. The first example showed that improved control of emissions of both total particulates and trace metals could be achieved by improved operating conditions (example, lower gas flows and temperatures) in existing devices and the use of additional control devices. All examples showed that in both waste gas streams and a selected waste water stream, the more volatile metals (zinc, cadmium, selenium, mercury, etc.) are the ones most likely to concentrate and are the most difficult to control. Further, the applied or planned methods of control were individually suited to each smelter.

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POLLUTION ABATEMENT IN THE METAL FINISHING INDUSTRY

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INTRODUCTION

Although there have been some significant advances in metal finishing waste treatment technology over the years, the extent of the progress has not been sufficient to meet the overall needs of the industry. Particularly today, with public concern and governmental pressure focussed on toxic pollutants, such as the heavy metals, chromate, cyanide, and fluoride discharged by metal finishing facilities, new and improved waste treatment technology is greatly needed by various segments of the industry. Moreover, the problem will be compounded as many municipal sewage plants accepting substantial amounts of metal finishing wastes upgrade to secondary treatment under governmental schedules, and the disposal of metal hydroxide sludges generated in the conventional treatment approach becomes more difficult as enforcement agencies intensify solid waste control.

The metal finishing industry in the United States is comprised of an estimated 20,000 facilities, including both job shops and captive installations associated with the automotive, aircraft, electronic, appliance, jewelry and other industries.

The primary environmental concern of the industry is water pollution. Waterborne wastes produced in metal finishing operations contain toxic pollutants, corrosive substances, oil, grease, surface active agents, organic solvents, nutrients, and settleable solids.

Metal Finishing Processes

The processing carried out in the industry may be classified as (a) cleaning for the removal of surface oils, grease, dirt, buffing compounds, etc. (b) removing undesirable surfaces such as oxides, rust, and scale by pickling; defective metal surfaces by stripping; and portions of metal surfaces by etching, and (c) electrochemical and chemical processing for surface coating a basis metal.

Metal surface preparation and cleaning are accomplished by (a) mechanical finishing activities, (b) organic solvents and alkaline cleaning solutions, and (c) pickling solutions. Mechanical operations such as tumbling, blast cleaning, polishing, or buffing produce solid impurities. Organic solvents and alkaline cleaning solutions are used to remove solid particles such as oil, grease, and dirt from workpieces.

Pickling is used extensively for the removal of scale, corrosion, and other undesirable surface conditions. Most pickling operations simply involve solution of the scale in acids such as sulfuric, hydrochloric, phosphoric, nitric, and hydrofluoric. Acid pickling on a large scale occurs in the steel industry, but considerable quantities of acids are also used in metal finishing facilities. Some pickling is also carried out with alkaline solutions.

Electroplating solutions are basically either acid or alkaline baths. Acid plating solutions contain free acid and heavy metals, usually chromium, nickel, copper, or zinc. Alkaline plating baths are mainly in the form of complex cyanide solutions. Some of the more significant cyanide plating solutions are copper, zinc, and cadmium.

Other important metal finishing operations include chromate conversion coating processes, anodizing, phosphate coating processes, stripping, etching, bright dipping, electro and chemical polishing, plating on plastics, and the application of organic coatings on metals.

Sources of Waste

In carrying out metal finishing operations, the workpieces are immersed in the bath and then lifted out, resulting in some loss of solution from the bath. The parts are either suspended from a moveable rack or are placed within a perforated barrel, depending on the size and shape of the pieces. Transfer of the parts from tank to tank may be done manually or automatically by conveyor. In performing the processing, the workpieces must be properly cleaned and conditioned before entering the metal finishing baths. Water rinses are employed after each treatment to prevent carryover of

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process solution, referred to as "dragout," into the next metal finishing operation.

The wastes produced in metal finishing facilities come mainly from the following sources:

1. The dumping of spent baths used for carrying out the various processing operations.
2. The rinse waters used to wash off process solution that has adhered to the surface or was entrapped in crevices due to the shape of the part.
3. Accidental waste discharges which can occur in practically every metal finishing operation in the plant. These wastes are usually significant where relatively little engineering effort has been directed toward preventing accidents.

Other sources of waste include plant and equipment cleanup, entrainment of mists in exhaust ventilation ducts, regenerants from ion exchange units, and sludges resulting from deposits in process tanks and the precipitation of contaminants from wastes.

IN-PLANT WASTE CONTROL

The methods available for the abatement of pollution may be divided into two general categories: (a) In-plant control techniques for conserving water and eliminating all unnecessary wastes, and (b) the installation of treatment and recovery processes to destroy or remove toxic and objectionable materials in the effluent.

Before considering treatment or recovery, the waste problem should be completely defined and, where feasible, reduced to the maximum extent possible by in-plant control techniques. In approaching the problem, a prime goal is to prevent the loss of chemicals into the wastewater. This will result in both a savings in the chemicals lost, plus the cost to treat these materials in the wastewater. Another major objective of in-plant control is to conserve water and reduce the volume of the waste, thereby decreasing intake water requirements as well as the size of the waste treatment equipment. In recent years, water conservation has been recognized to be a significant cost factor because of rising water costs, water scarcity in certain areas, and the increased cost of sewer rental charges.

In addition, process changes can sometimes be made to reduce or eliminate pollution without affecting performance or product quality. Some of the process changes made in metal finishing facilities to achieve pollution abatement are (a) the use of low or noncyanide plating solutions in place of high cyanide baths, (b) the replacement of phosphate in cleaning solutions, and (c) the substitution of mechanical cleaning for chemical treatments such as pickling.

An integral part of all industrial waste surveys that should not be overlooked is a complete reappraisal of the metal finishing operations carried out at the plant. This would involve an evaluation of the technical and economic features of both the processing and waste disposal aspects of the problem.

A breakdown of the various in-plant control methods for reducing contaminant loads and/or waste volume are shown in Tables 1 to 4. Basically, the reduction of dragout reduces the waste load; effective rinsing and water reuse practices conserve water and reduce the waste volume; and the prevention of spills, leaks, and other losses reduce the waste load and/or volume.

TABLE 1 REDUCTION OF DRAGOUT

Use of smooth, properly insulated racks designed with shapes for minimum carryover of process solutions.

Maintenance of racks to keep them in good condition, free of incidental metal build-up and corrosion.

Proper racking of parts for fast draining.

Scheduling sufficient time above the process tank for good draining.

Use of splash guards and drip boards for draining the solution back into the process tank.

Reduction of dragout by air blowoff, or movement of parts or tumbling of barrels above the process tank.

Use of wetting agents to permit increased drainage of process solution back into the bath.

TABLE 2 EFFECTIVE RINSING

Proper design of rinse tanks to provide adequate turbulence and prevent short circuiting of the water.

Use of air agitation in rinse tanks and/or agitation of the parts.

Use of nonrunning reclaim rinses as the first step to washing off dragout from parts.

Use of spray or fog rinses.

Use of multiple countercurrent rinsing.

Control of rinsing either manually or automatically by conductivity or flow of work (running rinse waters should be shut off when parts are not moving through the processing line).

WASTE TREATMENT

A variety of techniques are available for treating metal finishing wastewaters but the generally accepted procedure involves (a) separation of grease and oil, (b) oxidative destruction of cyanides, (c) reduction of chromates, (d) neutralization, (e) separation of the precipitated metal hydroxides, and (f) disposal of the sludge.

Other techniques that have achieved significant application for treating metal finishing wastewaters are (a) ion exchange to accomplish purification and re-use of strong baths and rinse waters, (b) the use of evaporation either alone or in combination with ion exchange to recover chemicals and purify rinse waters, and (c) the

TABLE 3 PREVENTION OF ACCIDENTAL AND OTHER LOSSES

Routine inspections to locate leaks.

Arrangement of all equipment and piping so it is in plain view and easily accessible.

Installation of float valves or alarm systems to prevent overflow.

Installation of walls or curbs around metal finishing baths to retain accidental losses or leaks from the tanks within enclosed areas.

Eliminating temporary connections in order to prevent accidental spills and discharging wastes into the wrong sewer.

Use of storage tanks, sumps, or pits located so as to save concentrated baths in case of leaks.

Use of above level filling lines in process tanks so operator can tell whether supply is on or off.

Education of personnel on good housekeeping practices, particularly in cleanup where every attempt should be made to minimize water use and salvage materials.

TABLE 4 RE-USE OF WATER

Use of rinse water effluents from some operations in others with lower rinse water quality requirements.

Use of steam condensate from heating operations as a source of pure water for solution make-up and rinsing.

Use of recirculating cooling water systems or re-use of the cooling water for rinsing in certain metal finishing operations.

Recirculation of washer waters from scrubbers.

Use of high quality water produced by many of the waste treatment methods for rinsing and/or bath make-up.

"integrated" or chemical rinse system for treating dragout prior to water rinsing. In addition, there are also a large number of metal finishing waste treatment techniques that have had only a somewhat limited application or are in various stages of development or demonstration.

A significant and troublesome problem in metal finishing wastewater treatment is sludge disposal. The metal hydroxides precipitated and settled from the wastewater are gelatinous and very difficult to dewater. The sludge also contains calcium carbonate and magnesium hydroxide formed from the hardness in the water supply, and the dirt that was on the parts or which resulted from the processing operations. Techniques available for concentrating or preparing these sludges for final disposal are thickening, vacuum or pressure filtration, sludge beds, centrifugation, and drying or incineration.

TABLE 5 METAL FINISHING WASTE TREATMENT TECHNOLOGY

Conventional
  Alkaline chlorination of cyanide
  Chemical reduction of hexavalent chromium to trivalent form
  Precipitation of metals as hydroxides
Ion exchange
Evaporation
Integrated chemical rinsing
Precipitation of hexavalent chromium
Electrolytic
Carbon adsorption
Carbon bed catalytic destruction of cyanide
Reverse osmosis
Electrodialysis
Ion flotation
Kastone process (hydrogen peroxide/formaldehyde oxidation of cyanide)
Ozone destruction of cyanide
Waste plus waste
Freezing processes
Sulfide precipitation of metals
Reduction of chromium by scrap iron (simultaneous cementation of copper may also be feasible)

Air pollution problems in the metal finishing industry result from (a) exhausting toxic and corrosive fumes and mists from processing baths, (b) solid particles from mechanical surface preparation activities, and (c) solvent vapors from cleaners and painting operations. Washers, packed tower scrubbers, cloth filters, cyclones, and solvent incinerators are used to prevent these contaminants from polluting the atmosphere.

The technology for treating metal finishing wastewaters presently in use or under development and demonstration is outlined in Table 5.

Conventional Treatment

Chemical destruction by alkaline chlorination is the commonly used method for removing cyanide from wastewater. The cyanide can be oxidized to the cyanate or further to nitrogen gas and carbon dioxide, depending on the requirements for discharge. Since cyanate reportedly is only about one-thousandth as toxic as cyanide, treatment to cyanate may be acceptable to regulatory agencies in some cases.

The alkaline chlorination process may be carried out either by adding chlorine gas and an alkaline compound to the wastewater, or by the use of hypochlorites such as sodium hypochlorite (NaOCl), calcium hypochlorite

$(Ca(OCl)_2)$ or bleaching powder $(CaOCl_2)$.

Alkaline chlorination of cyanide to form cyanates actually occurs in two stages. The first reaction is between chlorine and cyanide to form cyanogen chloride: this reaction is virtually instantaneous at all pH values. The second reaction involves the hydrolysis of cyanogen chloride to the cyanate. The rate of hydrolysis depends primarily on the pH and is relatively rapid at pH values above 10. At lower pH values, however, sufficient chlorine must be added to ensure an excess beyond that needed to oxidize the cyanide to cyanate so that the liberation of noxious cyanogen chloride is avoided.

The further oxidation of cyanate to nitrogen gas and carbon dioxide is slow and takes several hours or more at a pH over 10; however, this can be accomplished in a relatively short time at a pH below 9.

Wastes also contain heavy metal cyanide complexes in addition to the sodium cyanide. The alkaline chlorination process is effective in treating all of the common metal finishing cyanide complexes with the exception of nickelocyanides and ferrocyanides. If sufficient reaction time and excess chlorine are provided, even the nickelocyanides can be satisfactorily broken down. Since nickel plating is not carried out in cyanide solutions, the nickelocyanide complexes may be avoided by keeping these discharges out of the cyanide drains.

A one- or two-step process may be used to achieve complete destruction of the cyanide in metal finishing wastes. A single stage oxidation can be carried out by maintaining the pH between 8.5 and 9. Excess chlorine is needed to avoid the liberation of cyanogen chloride. The two-step process consists of first oxidizing the cyanide to cyanate at a pH above 10, and then reducing the pH to a value between 7.0 and 8 for the second stage oxidation.

The commonly used method for treating chromium-bearing wastes involves reducing hexavalent chromium to the trivalent form, which is then amenable to precipitation as the hydroxide. Normally, the pH of the waste chromium solution must be lowered since the optimum pH value for carrying out the reduction is between 2 and 3. Sulfuric acid is generally used to reduce the pH of the waste. The reducing agents most frequently used are sulfur dioxide, sodium bisulfite or metabisulfite, and ferrous sulfate.

After reducing the chromium and oxidizing the cyanide, all of the metal finishing wastes are usually combined and treated to precipitate the various heavy metals by adjusting the pH of the mixed effluent to a value between 8 and 8.5.

A batchwise or continuous operation may be employed for alkaline chlorination or chromium reduction. Batch systems are mainly suited for treating wastes from small and medium size metal finishing plants. The recommended practice for batchwise treatment is to have duplicate tankage. With two tanks, the wastes are collected in one while treatment is provided in the other. Continuous treatment is more practical for plants handling large volumes of wastes containing relatively low concentrations of contaminants. With continuous treatment, the size of the tankage is substantially reduced compared with that needed for batch operation, but provision must be made for handling process solutions that are discharged at intervals. Continuous treatment requires the use of automatic oxidation-reduction potential and pH controllers, both of which are also utilized in some cases for batch treatment.

Ion Exchange

Using ion exchange waste treatment systems in the metal finishing field is an accepted practice for certain types of effluents. Ion exchange is also used to a limited extent to treat a variety of other metal finishing wastes.

There are two basic applications of ion exchange for treating metal finishing wastes:

1. To purify the solution for re-use, remove heavy metal contamination from spent processing baths and reclaim or still rinses.
2. Demineralize individual or mixed flowing rinses and concentrate the dragout for chemical treatment or recovery to obtain a high quality water for re-use.

Ion exchange is widely used in the treatment of chromic acid process baths and rinses, and mixed rinse waters. A large number of commercial installations use this process.

Chromic acid plating, copper stripping, and aluminum anodizing operations are all adversely affected by a buildup of metallic contaminants in the processing bath. When the metallic impurities reach a certain level, it becomes necessary to replace either a portion or the entire bath with chromic acid. The problem of disposing of these baths may be overcome by passing the solution through a cation exchange unit operating on the hydrogen cycle as illustrated in Figure 1. The metal cations are removed from the bath and exchanged for hydrogen ions, thus reforming the chromic acid. Although chromic acid anodizing solutions can be

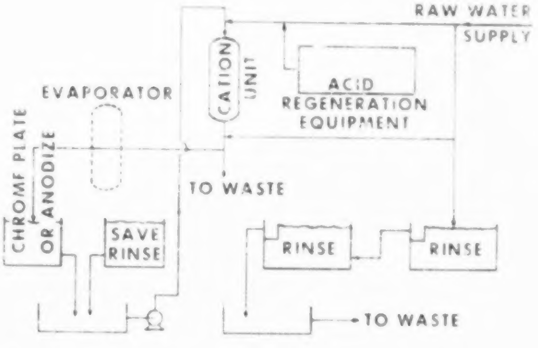

Figure 1. Cation exchange unit for chromic acid recovery.

treated directly, chromic acid plating and copper stripping solutions must be diluted and subsequently concentrated after ion exchange treatment. The high chromic acid concentration in these baths prevents effective removal of the metallic impurities and causes oxidative degradation of the resin. Highly crosslinked and macroreticular resins are used to treat chromic acid solutions due to their ability to withstand oxidizing conditions.

Ion exchange is also applied commercially to reconstitute other processing baths including sodium dichromate passivating or chromatizing solutions, phosphoric acid solutions used to pickle steel or bright finish aluminum, and acetic acid solutions used to pickle magnesium.

Metal finishing rinse waters are treated by ion exchange for (a) pollution control, (b) water re-use, and (c) chemical recovery or concentration. A hydrogen cation and hydroxyl anion exchange column are used to demineralize the rinse water. Where it is feasible to segregate the chromic acid, cyanide, and other rinses, metal may be recovered by treating the individual rinse waters. For example, when treating chromic acid rinse waters, the sodium chromate regenerant from the anion exchanger can be passed through the hydrogen cation exchanger to reform chromic acid. When treating nickel plating rinse waters, the sulfuric acid regenerant discharged from the cation exchanger is a relatively concentrated nickel sulfate solution. When treating mixed rinse waters, the contaminants are concentrated to very small volumes in the regenerant solutions, which are then easily and effectively treated by conventional chemical practice.

When treating mixed rinse waters, cyanide contaminants pose some problems and require special consideration. Most serious is the poisoning of the anion resin by the adsorption of tightly held cyanide complexes that are difficult to regenerate off the exchanger bed. Conventional demineralization has shown little or no poisoning effects if the cyanide level is low. Poisoning of the anion resin will occur when the cyanide exceeds a certain level, depending on the contaminants present. A two-stage regeneration procedure and a three-bed system consisting of a strong acidic, weakly basic, and strongly basic exchanger permit effective treatment of cyanide rinse waters.

The use of ion exchange is a common practice for recovering the precious metals from rinse waters. Although the tightly held anionic metal complexes cannot be eluted from the exchanger, the high price of gold, platinum, and other precious metals makes incineration of the resin a practical recovery technique.

Evaporation

Evaporative recovery of processing chemicals from rinse waters has become an established method for controlling pollution in the metal finishing industry. This approach, however, has found only limited application. To be economical, it is generally necessary to apply evaporation to relatively concentrated rinses, such as those produced in still or reclaim tanks and those from countercurrent rinsing. The technique is attractive in operations where the amount of dragout is large and waste flows are small. Another important factor is the cost of the processing chemicals to be recovered. The evaporative technique requires segregation of the wastes by compatible types and the use of various means for excluding or removing impurities.

Evaporative recovery concentrates the chemical dragout in the rinse water to bath strength and returns this concentrated solution to the process tanks. The evaporated water is re-used in the rinse system, thereby evaporated water is reused in the rinse system, thereby providing a high quality water for rinsing and minimizing the water intake to the facility.

In metal finishing systems, dragout naturally purges baths of any contaminants resulting from the processing operation. Buildup of impurities in evaporative recovery operations may be prevented by the incorporation of techniques such as ion exchange, precipitation, and activated carbon treatment.

In closed-loop operation (Figure 2), the system is designed to recover 100 percent of the processing chemicals lost in the dragout for re-use in the metal finishing operation. No external rinse water is added except that required to replace the loss from atmospheric evaporation. The only chemicals supplied to the metal finishing bath are those needed to replace what is actually deposited on parts and to replace that lost by spillage or accidentally. Although total closed-loop control represents an idealized system, it has been closely approximated in many installations.

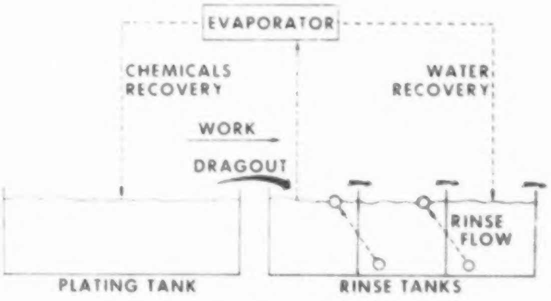

Figure 2. Closed-loop evaporative recovery system.

Often, the favorable economics of closed-loop evaporative recovery does not apply because a processing line has an insufficient number of countercurrent rinse tanks. Generally, at least three rinse tanks are needed to make evaporative recovery of dragout effective and economical. The number of rinse tanks determines the amount of steam required for evaporation, which is the largest cost for recovery.

When a layout of a metal finishing facility does not meet the conditions for a closed evaporator loop, a partial recovery system referred to as open-loop evaporation may still be attractive. In this operation, the water from the first rinse tank following the metal finishing bath is circulated through the evaporator. The concentrated solution is returned to the processing tank and the evaporated water is re-used in rinsing. A second rinse tank is furnished with a separate supply of water which, after rinsing, is discharged to waste. This rinse water effluent contains only a very small portion of the "dragout" because the bulk of the solution carried out of the bath enters the first rinse tank and is recovered in the evaporative system. The small fraction of dragout solution entering the second rinse tank can be treated by some method other than evaporation before sending it to the sewer.

Integrated Treatment

The integrated system has gained considerable acceptance in the United States in recent years and is now an established method for treating process solutions dragged out of metal finishing baths. The basic concept is segregation and treatment of the waste at the source. Treatment is accomplished by integrating a chemical washing operation as the first step in the rinsing sequence. Chemical washing involves simultaneous removal and treatment of the film of processing solution adhering to the parts removed from the metal finishing bath.

The integrated system incorporates a chemical wash tank immediately following the metal finishing operation before the part enters the water rinsing sequence. In some cases, the chemical washing operation may follow a reclaim still rinse tank. The chemical solution is continuously recirculated through the wash tank and a larger reservoir tank as shown in Figure 3. In the wash tank, the treatment solution both physically removes the dragout and at the same time chemically reacts with the contaminants. The reservoir tank is a buffering component in the system for neutralizing shock loadings caused by sudden and irregular changes in the quantity of process solution dragged into the wash tank. It also serves as a clarifier for settling out the insoluble metal oxide and hydroxides formed in the first stage of the reaction, as well as a retention tank to provide adequate time for the desired chemical reactions, such as the oxidation of cyanides or the reduction of chromates. Several wash tanks treating similar types of dragout solution can be served by a common reservoir tank. As an example, the same chemical wash may be used after various cyanide plating or processing operations or after chromate conversion coating operations involving different basic metals.

Since the chemical rinse solution is continuously recirculated and not wasted in the integrated system, a much higher concentration of chemicals can be used than is needed to react with the dragout during the time the workpieces are washed in the treatment solution.

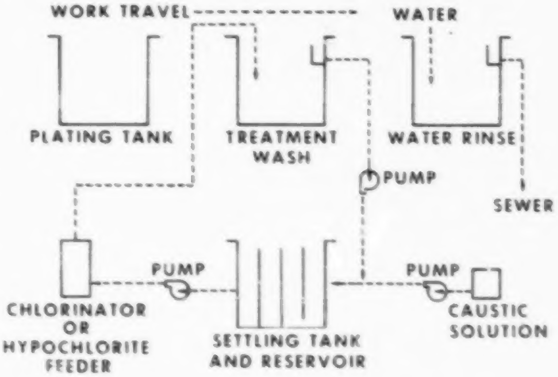

Figure 3. Integrated waste treatment system for cyanide plating effluents.

The integrated system produces relatively high density sludges compared with conventional chemical treatment. In addition, a substantial portion of the freshwater rinse may be re-used since there is no direct addition of treatment chemicals and the carryover from the chemical wash tank is relatively dilute and nontoxic.

Over a period of time, harmless waste treatment reaction products, such as sodium chloride, sodium carbonate, and sodium sulfate, slowly build up in the chemical wash solution. No problems are normally encountered, however, because solution is dumped infrequently and does not contain any toxic materials.

Precipitation of Hexavalent Chromium

Hexavalent chromium also may be directly removed from metal finishing wastewaters by precipitation as an insoluble salt of chromic acid. The treatment method generally involves the use of barium compounds for the precipitation of insoluble barium chromate.

Rigid chemical control is necessary in carrying out the operation to ensure the addition of the correct amount of barium chloride or other compound because of the generally toxic nature of barium salts. In addition, the sludges produced in the process are toxic and may present some disposal problems. Direct precipitation of chromium has only been applied to a very limited extent.

Electrolytic Treatment

For strong baths, the electrolytic decomposition of cyanide solutions is economically feasible. Spent plating solutions, strip baths, and cyanide dips fall into this category. The technique is useful for reducing concentrated solutions to a point where a secondary treatment may be employed to remove the remaining cyanide satisfactorily.

Electrochemical treatment of metal finishing rinse wastes has not been practical because of the low conductivity of these effluents. However, a new electrolytic processing technique has been introduced that uses a bed of carbon particles between the electrodes to overcome the high resistance of the rinse waters. The system is designed to treat either cyanide or chromate rinse waters.

The individual particles that make up the bed are said to exhibit bipolar properties under an applied D.C. current. Each particle has an anode portion at which oxidation can occur and a cathode portion at which reduction can take place.

In treating cyanide rinse waters, the cyanide is oxidized to nitrogen and carbon dioxide, and the metal ions are both electro-deposited at the cathode sites and precipitated as the oxide or hydroxide at the anode sites. In some cases, caustic may have to be added to the effluent for complete precipitation of the heavy metals. The treatment of chromium-bearing rinse waters involves a reduction of the hexavalent chromium to the trivalent form at the cathode sites but no precipitation will occur in the beds because of the low pH of the waste. The trivalent chromium and other heavy metals are subsequently precipitated by the addition of alkali.

A number of plants are employing the new electrolytic approach to treat cyanide and chromium-bearing metal finishing rinse waters.

Carbon Adsorption

A recently completed laboratory and pilot plant study has resulted in the development of an activated carbon adsorption process for treating chrome or cyanide rinse waters from metal finishing shops. Although the technical feasibility of the process has been established, further study and refinement of the stripping operations are needed as the carbon bed experienced a loss of chromate capacity and required successively longer periods for eluting the cyanide over a somewhat limited number of treatment cycles.

Carbon Bed Catalytic Destruction of Cyanide

A new system that uses a granular activated carbon bed to catalytically destroy cyanide has recently moved out of the development and demonstration stage into commercial application. The process is designed to continuously oxidize cyanide to carbonates and nitrogen compounds by adding a copper catalyst and air to the raw waste and then passing the solution through the carbon column. The presence of copper ions results in the formation of copper cyanide complexes that are adsorbed to a much greater extent than cyanide, permitting higher flow rates through the column. The copper also aids in cyanide oxidation and accelerates cyanate hydrolysis to end products that combine with the cupric ion to form precipitates of copper carbonate and copper hydroxide – amine compounds that remain in the carbon bed. After some period of time, the carbon bed either must be replaced or the copper precipitates removed by dissolution with acid.

Membrane Processes

The use of reverse osmosis and electrodialysis as methods for treating metal finishing rinse waters is in the development, demonstration, and early application stage. These membrane techniques accomplish pollution abatement by (a) purifying the rinse water for re-use, and (b) concentrating the chemicals for return to the bath or for convenient subsequent treatment or disposal.

Electrodialysis involves the transport of ionic species through membranes by the application of a D.C. current. Compartments formed by a cation and anion membrane are arranged in a stack configuration between electrodes. As the rinse water flows through every other compartment, the cation exchange membrane permits the passage of cations and rejects anions, while the anion membrane allows the passage of anions and rejects cations, thus purifying the rinsewater while forming a concentrate in the adjacent compartments.

In reverse osmosis, pressure is used to force pure water through the membrane while the chemicals are rejected and concentrate in the rinsewater. Reverse osmosis equipment is available in plate-and-frame, tubular, spiral-wound, and hollow fiber types.

Along with the application of membrane systems, an important part of the investigations underway involves a continuing search for the most appropriate membranes to treat the various types of rinsewaters. The development of membranes with improved properties will have an important bearing on the success and acceptance that reverse osmosis and electrodialysis receive in the metal finishing industry.

Ion Flotation

The use of ion flotation for treating metal finishing rinse waters is in the early development stage. The technique involves the use of organic collectors having surface active properties and an inorganic group that ionizes in aqueous solutions. The contaminant ions such as chromate or complex cyanides are removed from the solution by the collector that attaches to small rising air bubbles that form a froth at the surface.

Hydrogen Peroxide/Formaldehyde Destruction of Cyanide

A new process referred to as "Kastone" uses a proprietary peroxygen compound in the presence of formaldehyde to oxidize cyanide to cyanate in rinsewaters from zinc or cadmium metal finishing operations. During the treatment, which is designed for batchwise operation, the zinc, and/or cadmium, or both precipitate and are easily removed by filtration. The major components in the rinse water after treatment are the cyanate ion, ammonia, and glycolic acid amide. This approach has been finding some acceptance by the industry, particularly in small metal finishing shops discharging to municipal sewers.

Ozone Destruction of Cyanide

Ozone is a suitable oxidant for cyanide, with the final reaction product being substantially cyanate. The oxidation of cyanide to cyanate by ozone is rapid and practically instantaneous in the presence of a trace of copper, but oxidation of the cyanate is relatively slow.

Ozone is generated in commercially available equipment and must be introduced in a manner to ensure intimate contact with the entire waste solution. This may be done in tray or packed columns or by dispersion of the ozonized air through diffuser plates at the bottom of the chamber.

This treatment method has found application in a few plants and has the advantage of not adding any constituents to the water. The cost of producing ozone is a major factor in the economic feasibility of the process, which has become more attractive in the last few years because of the reduced cost for generating ozone.

Waste Plus Waste

A new approach to removing cyanides and metals from metal finishing wastes has recently been developed in bench scale studies conducted at the U. S. Bureau of Mines in Rolla, Missouri. The method simply involves slowly blending the acid wastes from the facility into the alkaline cyanide wastes in a well-mixed closed reactor. At a pH value near 7, the heavy metals and cyanide in the blended waste precipitate and are easily filtered from the solution. The applicability of the technique will depend largely on the relative amounts of cyanide and acid wastes produced at the plant as well as the particular heavy metals present. Heating the metal cyanide precipitates in the presence of air results in the formation of relatively stable metal oxides.

Freezing

Development work on two types of freezing processes for recovering chemicals while simultaneously purifying metal finishing rinse waters for reuse has recently been reported. In one case, bench scale investigations have been conducted on a freeze drying process in which frozen waste droplets are formed in a refrigerant solution followed by sublimation of the water from the crystals in a vacuum chamber. In the other, pilot plant investigations have been carried out on a process in which cooled metal finishing wastes are frozen in direct contact with an immiscible fluorocarbon refrigerant. The ice crystals, which are virtually pure water, are cleaned to remove chemicals adhering to their surface in a unique countercurrent washer. The concentration can be carried to the point of saturation where the salts precipitate out of solution.

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CONTROL AND PREVENTION OF MINE DRAINAGE

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SOURCE

Associated with most ore and coal bodies are sulfides and/or sulfosalts. The most common sulfides are the iron, i.e., pyrite (FeS_2), pyrrhotite, and marcasite. In addition, there are numerous other sulfides and sulfosalts. The general formula for sulfides is AmXn where A consists of the metallic elements or sometimes arsenic, antimony and bismuth (1). The general formula for sulfosalts is AmBnXp. The elements found in sulfides and sulfosalts are shown in Table 1. The diversity of the combinations of the chemical elements is tremendous, over 125 occur naturally. Thus, a potential of trace metals in discharges from mines is always present.

Iron sulfides when exposed to air and water oxidize to form ferrous iron, sulfate, and hydrogen (equation 1). Pyrite also can be oxidized by ferric iron (equation 2). The reaction may then proceed to form ferric hydroxide and more acid (equations 3 and 4).

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4 \qquad (1)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2S_4{}^{2-} + 16H^+ \qquad (2)$$

$$4FeSO_4 + 2O_2\ 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \qquad (3)$$

$$Fe(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4 \qquad (4)$$

As seen by the equations, for each mole of iron sulfide oxidized, four moles of acid are produced. The result is the lowering of the pH of the water draining from the material. At the lower pH levels, the heavy metals are more soluble and enter into the solution. As the iron sulfides oxidize, the associated sulfides and sulfosalts are either oxidized or exposed to conditions conducive to their breakdown with the release of diverse metallic and nonmetallic ions to the environment.

Under certain proper conditions, any of the ions shown in Table 1, may be present in the drainage. For example, the breakdown of chalcopyrite ($CuFeS_2$) would release copper and iron. However, gold, silver, and selenium are often associated with chalcopyrite and also may be present. The metal ions in the drainage will depend on the sulfide and sulfosalts present, the materials associated with the area (clays and minerals), and the chemical characteristics of the metal ion and water. The solubility of the metal is a primary factor.

TABLE 1 ELEMENTS IN SULFIDES AND SULFOSALTS*

Sulfides (AmXn)					
A				X	
Ag	Fe	Pb	As	S	As
Cu	Co	Hg	Ni	Se	Te
Zn	Cd				
		Rarely Found			
Ru	Sb	Sn	Ti	Sb	Bi
Mn	Bi	Mo	Au		
Ca	Pt	W			
Sulfosalts (AmBnXp)					
A	B	X			
Cu	As	S			
Ag	Sb				
Pb	Bi				
Sn	Sn				

*Reference 1.

Mine drainage occurs not only from the mine itself, but also from waste dumps and tailings areas. The latter two sources often have a higher concentration of metal ions because the sulfides have been concentrated in these locations. In Table 2, examples of mine drainage are presented.

PREVENTION

The ultimate solution to the mine drainage problem is preventing its formation. As noted in equations 1 through 4, the reaction is dependent on air (oxygen) and water coming in contact with the sulfides. In addition to

TABLE 2 EXAMPLES OF MINE DRAINAGE

Source	Tailings pond Ontario*	Mine adit Colorado	Mine adit Idaho	Mine adit Montana
pH	2.0	2.6	3.2	–
SO_4, mg/l	7,440	1,610	–	–
Acidity, mg/l	14,600	–	–	44
Fe^2, mg/l	1,450	5	–	2
Fe^3, mg/l	1,750	213	–	16
U, mg/l	7.2	–	–	–
Zn, mg/l	11.4	17	18.8	0.14
Ni, mg/l	3.2	0.46	–	–
Co, mg/l	3.8	–	–	–
Cu, mg/l	3.6	3.9	0.06	0.12
Mn, mg/l	5.6	8.0	–	1.2
Al, mg/l	588	77	–	0.2
Hg, mg/l	–	–	0.03	<0.005
Pb, mg/l	0.67	0.3	2.5	0.02
Cd, mg/l	0.05	0.07	0.05	0.001
Li, mg/l	0.07	–	–	–
V, mg/l	20	–	–	–
Ag, mg/l	0.05	<0.01	–	–
Ti, mg/l	15	–	–	–
Mg, mg/l	106	–	–	3.7
Ca, mg/l	416	–	–	11.2
K, mg/l	69.5	–	–	–
Na, mg/l	920	–	–	6.7
As, mg/l	0.74	0.07	0.07	<0.01
P, mg/l	5	–	–	1.7

*Reference 1.

water being a reactant, it serves as the transport media for the metals. All prevention techniques are based on excluding water and/or air from the mining environment.

Air

Air is necessary during the active operation of an underground mine. After the ore has been extracted, excluding air should be an integral part of the mining plan. As areas are worked out, blockages should be made to prevent air from entering that section of the mine. Mines should be developed downdip so that they flood when abandoned. In this manner, water serves as an oxygen barrier. Injecting solid material into the mine, such as stope filling, should be encouraged and expended. Not only can the mine drainage problem be decreased by blocking the flow of air, but a solid waste disposal problem can be resolved simultaneously.

Sealing adits to prevent air from entering an underground mine has been in practice in the coal fields since the 1920's. This procedure, at its best, has been only marginal. Seals can be built to prevent air from entering the adit, but air reaches the mine readily through the fractured outcropping and overburden. With each change in barometric pressure, air is pumped in and out of the mine. Air sealing may be an acceptable method in some hard rock mines that have tight outcrops and overburdens.

Bulkhead or hydraulic mine seals have been shown to be successful (2). For this method a seal is built in the adit and the outcrop is grouted to prevent water from leaving the mine. In time, the mine workings are flooded and oxygen is excluded from the sulfides.

Excluding oxygen from the active surface mine is impossible. Usually there is a delay between the time the sulfides are exposed to air and acid mine drainage is formed. High sulfide bearing material should be exposed for the shortest time possible. As part of the mining operation, this material should be covered with material containing little or no sulfides. The cover material acts as an oxygen barrier. Wind and diffusion are the only driving forces for moving air through the cover material to the sulfides. The cover material should be vegetated with grasses, legumes, shrubs, forbs, etc. Not only does the vegetation serve to stabilize the cover material and prevent it from eroding, but upon dying, it decays and acts as an oxygen absorber.

Waste dumps at mines are major sources of mine drainage and should be constructed to prevent air movement into them. Sound techniques are compacting waste material as it is placed and sandwiching layers of compacted clay between layers of waste. The slopes of the dumps should be kept to 33 percent or less to prevent wind from driving air into the pile. Upon abandonment, the surface of the pile should be sealed with an air barrier. Although many different materials have been evaluated, soil still remains the best. As in the case of surface mines, the surface should be vegetated.

Water

Enough water is usually available in the moist air within an underground mine or within the material itself in a surface mine or waste dump that the requirement for the formation of mine drainage is met. The other function of water is as a transport media. It flushes the oxidation products from the sulfide and carries them into the environment. By controlling the water, these products can be contained.

Provisions should be made to prevent water from entering the mining environment, except where it is to be used for flooding and an oxygen barrier. Diversion ditches, dewatering of the working, and sealing of fractures are just a few of the methods available. Water that does enter the workings should be removed as rapidly as possible.

CONTROL

Several methods are available to treat the mine drainage that cannot be prevented.

Neutralization

The most commonly used method for treating acid mine drainage and removing heavy metals is neutralization. A typical system would include adding an alkaline reagent, mixing, aerating, and removing the precipitate. Alkaline reagents that may be used are ammonia, sodium carbonate, sodium hydroxide, limestone, and lime. In most cases, lime is used because of its lower cost and higher reactivity.

Most heavy metals tend to precipitate as the pH is raised. In Table 3, typical pH ranges at which various metals will precipitate are presented. Metals such as copper, zinc, iron, aluminum, manganese, nickel, and cobalt can be reduced to low levels, less than half mg/1, with pH adjustment, precipitation, and solids separation. Cadmium, lead, and mercury precipitation may be incomplete and other chemical treatment will be required (3).

In removing iron, aeration is used to convert Fe II to Fe III to take advantage of the precipitation of Fe III at a lower pH.

TABLE 3 PRECIPITATION OF HEAVY METALS BY pH CONTROL

Ion	pH Range	Ion	pH Range
Fe III	3.5–4.5	Na II	7.0–8.0
Al III	4.5–6.0*	Cd II	7.0–8.0
Cr III	5.5–6.5	Hg II	7.5–8.5
Pb II	6.0–7.0	Fe II	7.5–9.0
Cu II	6.5–7.5	Mn II	8.5–9.5

*Note: Al will become soluble again at pH greater than 7.5.

In most cases, lime is used for neutralizing. Except for limestone, it is the cheapest reagent, and it also reacts rapidly. Its disadvantage is that voluminous sludge is produced. Although limestone is cheaper and produces a denser sludge, it is not effective above a pH of 6.5 because of the slow attack of limestone by acidity at higher pHs. Two-stage treatment with limestone followed by lime appears to offer the advantages of both reagents. The Japanese have studied this process on discharges containing iron, zinc, and manganese (4), and have a plant that employs it for zinc, cadminum, and iron (5). EPA has studied its use on coal acid mine drainage (6). Two or more stage treatment with the proper selection of pH can be used to separate heavy metals with subsequent recovery (3, 7).

Although neutralization can be used to remove heavy metals and a portion of the sulfate, the resulting water is high in dissolved solids and sulfate. The disposal of the sludge is also a problem.

Ion Exchange

Various ion exchange schemes have been applied to the treatment of coal acid mine drainage (8). These schemes can upgrade the water quality to potable use. Modification can be incorporated to recover heavy metals. Ion exchange has not received wide acceptance because of difficulties encountered with resin fouling, interfering ions, limited loading capacity, cost of operating, and disposal of regenerating solutions. Further development is needed.

Reverse Osmosis

Reverse osmosis (R.O.) has effectively removed multivalent ions from mine drainage. Table 4 presents data from the treatment of coal mine drainage. All heavy metals should be removed at about this same level (99 percent or better). Reverse osmosis is a concentrating process in which the pollutants are contained on one side of a membrane while the water passes through. Water recoveries (percent of water feed to unit that is available as treated water) have been as high as 90 percent. Water recovery is limited by the precipitation of material on the membrane when they have been

TABLE 4 TREATMENT OF MINE DRAINAGE BY REVERSE OSMOSIS

Element	Removal–%
Ca	98 –99.8
Mg	98.5–99.8
Fe, total	98.5–99.9
Al	91.7–99.2
Mn	97.8–99.1
Cu	98.7–99.5
SO_4	99.3–99.9
Acidity	81.0–91.7
Specific conductance	95.0–99.9

concentrated beyond the materials saturation point. Calcium sulfate is usually the first material to be precipitated in mine drainage. Equations have been developed to predict the highest water recovery allowable under any influent condition (9, 10).

Since R. O. is a concentrating system, the disposal of the waste stream is a major problem. The concentrated heavy metals in the waste stream would lend themselves better to processes for recovering the metals. For systems where recovery is not practiced, EPA has developed a system whereby the waste stream is neutralized, the sludge removed, and the neutralized water returned to the influent of the R. O. unit. This system has been named "Neutrolosis" and has obtained water recoveries in excess of 99 percent (11).

Cementation

Taking advantage of the electromotive force between metals can be used to remove and recover metals from mine drainage. A notable example is the recovery of copper by passing the copper bearing water through shredded iron. The copper is "cemented" to the iron. The process may have application in other situations (3).

Electrolytic

With the use of electrodeposition processes, several metals, such as copper and iron, can be removed from mine drainage. The metal is deposited on the cathode of an electric cell from which it can subsequently be recovered. This method is only applicable to waters with very high concentrations of the metal.

Electric cells can also be used to oxidize metals from the plus three state to the plus two state before neutralization or other treatment. Studies have been made on converting ferrous iron to ferric iron in the acid state by this method (12).

SUMMARY

Many different heavy metals can be found in mine drainage because of the variety of ores and minerals associated with mining operations. The first approach to control heavy metal discharges should be preventing the formation of the mine drainage. Many ways are available for controlling air and water in mining operations. For the mine drainage that cannot be prevented, several treatment methods are available, some of which offer ways of recovering the metals.

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CONTROL OF PARTICULATE LEAD EMISSIONS FROM AUTOMOBILES*

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INTRODUCTION

Recent proposed regulations concerning fuels and fuel additive content by the U.S. Environmental Protection Agency (EPA) call for the general availability of one grade of lead-free fuel by July 1, 1974 for use in 1975 and later model cars equipped with catalytic devices (1). In addition, the proposals call for a scheduled reduction of the lead content of regular and premium grades of gasolines. Under this reduction schedule the maximum content would be limited to 1.25 grams of lead per gallon by January 1, 1977. EPA justified this reduction schedule on the basis that automotive emissions of lead should be reduced sufficiently to reduce the lead content of the air in urban areas by 60 percent by 1977. The implication is that such reductions are best accomplished by regulating the lead content of gasoline. However, there is an alternative approach which is more consistent with the position that control regulations should be based on tail pipe emission standards rather than regulation of fuel and fuel additive content. Exhaust particulate lead traps used on cars burning leaded gasoline have demonstrated the ability to significantly reduce motor vehicle lead emissions (2, 3).

During the past seven years a number of different studies have been conducted at duPont to develop methods and means to measure, characterize, and control vehicle exhaust particulate as well as gaseous emissions. Habibi has developed and described the use of two different vehicle exhaust particulate sampling systems (4). One measures the total particulate lead emission rate from cars operating under normal driving conditions. The second system, based on a proportional sampling principle, provides size classification, and other characterization on a representative sample of the particulate matter. A third approach to measure and characterize vehicle exhaust particulate has been described by Pierrard and Crane (5). They measured the atmospheric visibility and soiling effects of exhaust particles from cars using different gasolines. In addition to using the Habibi sampling procedures, they measured the effect on the atmosphere of exhaust particulate emissions from cars driven in a 1-1/4-mile long unused Pennsylvania turnpike tunnel. All three of these exhaust particulate measurement techniques were used in evaluating the efficiency of the trap systems described in this paper.

A number of trap systems for control of automotive exhaust particulate have been developed by duPont and reported previously (2). Brief descriptions of these systems are included in this paper along with new data on the total lead removal efficiency of lead traps for different size lead particles, and airborne lead emissions from production and trap-equipped cars driven on the road in the unused Pennsylvania turnpike tunnel. In addition, one trapping system was combined with a gaseous emission control system to provide control of all gaseous and particulate emissions from a vehicle. The development and performance of a new type of lead trap, designed to replace the exhaust muffler of existing cars on the road, last the life of the vehicle, and reduce the airborne lead emissions from cars by greater than 65 percent is presented in this paper.

EXHAUST PARTICULATE EMISSIONS – TEST METHODS

The particulate matter emitted from automobiles is a complex mixture of leads, salts, iron as rust, alkaline earth compounds, soot, carbonaceous material, and tars. Some of the particulate matter found in the vehicle exhaust is generated in the engine combustion chamber and is nucleated and agglomerated in the car's exhaust system before it is emitted from the tail pipe. On the other hand, a large portion of the particulate material generated in the engine subsequently deposits on various surfaces of the exhaust system. Later, this deposited material flakes off and becomes re-entrained in the exhaust gas to be emitted from the car. Thus, many factors, such as previous history of car operation, age of exhaust system, mileage, age of car, type of fuel and mode of vehicle operation during test, can affect the total particulate emission rate.

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The complexity of the particulate emission process makes the task of measuring the amount of emitted lead very difficult. Satisfactory sampling cannot be accomplished, for instance, by simply inserting a probe in the tail pipe of an operating vehicle and collecting the effluent for a short time (3). Such sampling procedures can result in the collection of samples with abnormal particle size distributions as well as unrealistic total particulate emission rates. Factors contributing to these discrepancies include nonuniformity of the particulate profile in the tail pipe, nonproportionality of the sample, and inaccurate sampling of large particles. Furthermore, with a short test interval and without conditioning of the vehicle before the test, the emission rate may be abnormal also.

Satisfactory methods to provide meaningful data on particulate emission rates must (a) employ a suitable sampling system for isolating and collecting particulate matter, (b) utilize vehicle driving patterns which simulate average vehicle operation and are important in affecting particulate emission processes, (c) provide for tests of adequate duration to insure good repeatability, and (d) employ a vehicle conditioning period prior to a particulate emission test. Three different techniques were used to monitor the particulate lead emission rates of the production and emission control-equipped vehicles discussed in this paper.

Total Lead Emissions

All "total" lead emission rates reported in this paper were measured with a total exhaust filter (4) attached to the vehicle tail pipe while the car was operated on a programmed chassis dynamometer (PCD) according to the Federal mileage accumulation (Modified AMA) schedule (6).

The total exhaust filter shown in Figure 1, which mounts directly on the tail pipe of the car is a cylindrical drum, 18 inches in diameter, 24 inches long, and packed with a high efficiency fiberglass medium. The total vehicle exhaust flows through the filter which is designed to give a low pressure drop across the filter – less than two inches of water at 70 miles per hour cruise. The pressure drop across the filter increases with accumulation of material on the filter. In practice the filters are removed when pressure drop exceeds six inches of water so that the use of the filter does not affect the vehicle operation. This increased pressure drop corresponds to about 500 miles of continuous hot-cycle operation for a production vehicle and as much as 2,000 to 4,000 miles with a trap-equipped car. However, the filter is usually changed every 1,000 miles for the latter vehicle to provide more accurate data and as a convenience in the operation.

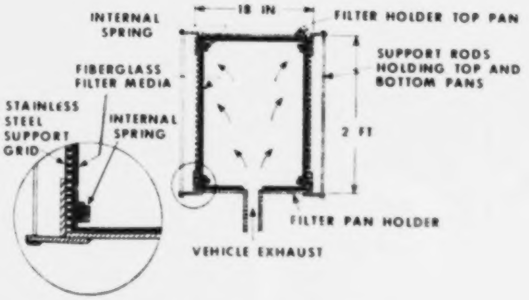

Figure 1. Total exhaust filter.

After each test, the filter unit is disassembled and lead on the filter medium is extracted in hydrochloric acid. The lead deposited on the inlet pipe and internal parts of the holder is extracted with an aqueous solution of the tetrasodium salt of ethylenediamine tetraacetic acid. These solutions are analyzed for lead by atomic absorption. The efficiency of this filter for exhaust lead removed has been tested in a number of experiments reported previously (4). Under normal driving conditions, the unit is 99 percent efficient for lead removal.

Lead Particle Size

The exhaust particulate sampling system developed by Habibi (4) and shown in Figure 2, was used in this study to determine the amount of lead emitted as a function of lead particle size. In this system, the total exhaust gas from a vehicle operating on the PCD is introduced into a duct 22 inches in diameter and 40 feet long. The exhaust is diluted with filtered ambient air using the constant volume proportional sampling principle. The average dilution of the exhaust during the test cycle was 35 to 1, which is sufficient to prevent condensation and to cool the exhaust to near ambient temperatures. A time of approximately five seconds is required for the exhaust-air mixture to travel the length of the tunnel and reach the sampling station.

To measure lead particle size, an isokinetic sample of the uniformly mixed aerosol is taken at the sample station using an Andersen sampler (4) and a Monsanto Impactor (4). These two impactor units are used

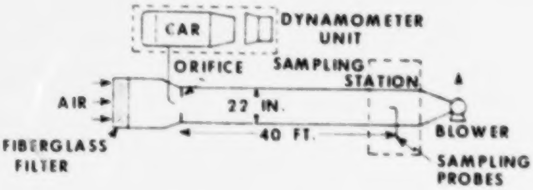

Figure 2. Proportional sampling system for exhaust particulate matter.

simultaneously to provide a wide size distribution measurement of exhaust lead particles over the range of 0.3 to 9.0 microns equivalent diameter. Particles smaller than 0.3 micron equivalent diameter are collected on an absolute filter downstream of each impactor unit. As discussed by Habibi (4), there is some gravitational settling of the large particles present in the exhaust along the tunnel as well as some turbulent deposition of particles on the tunnel walls. The amount of this particulate lead deposited in the tunnel is determined after each run and is included in the greater than nine micron equivalent diameter size fraction. Each size data point reported in this study represents the average of at least three separate tests. Each test was of about 200 miles duration and was conducted on the PCD according to the Federal mileage accumulation schedule.

Airborne Lead Emissions

"Airborne" lead was determined by measuring the amount of lead remaining in the air in a sealed turnpike tunnel after driving vehicles back and forth on the tunnel roadway (5). Limited measurements have been made to determine the size distribution and average particle size of the "airborne" lead remaining in the tunnel after driving production vehicles through the tunnel. These data show that the average lead particle size is approximately 0.25 micron mass median equivalent diameter which as discussed later is the average size of the lead particles found in urban atmospheres.

For each test, the car was started cold after a 16-hour soak period and manually driven back and forth over a fixed course (Figure 3) for a total of twenty-four 7-mode Federal test cycles (6) with the aid of an audiotape prompter. An absolute filter sampler mounted on the roof of the test car collected a spatially integrated sample of airborne tunnel particulate matter over the driving course during each driving period. Prior to conducting the test, the car was conditioned by driving a total of fifty 7-mode Federal test cycles on the road. The turnpike tunnel was conditioned prior to each test as previously reported by Pierrard and Crane (5). This conditioning consisted of flushing the tunnel with clean ambient air for about one hour prior to each test or for such time as required to lower the tunnel carbon monoxide concentration and light scattering coefficient to the same level as the outside air.

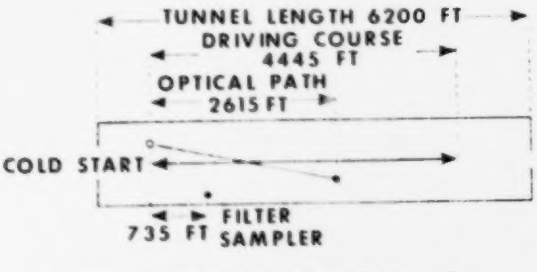

Figure 3. Pennsylvania Turnpike tunnel.

Since the test conditions were the same for all cars, the actual reduction of airborne lead achieved by use of trap-equipped cars rather than production vehicles can be determined directly by comparing the amount of lead collected by the roof-top filter during the operation of a trap-equipped vehicle to the amount collected during the operation of a production vehicle. Such results, after correcting for a blank and normalizing for the volume of air sampled, are discussed later.

In addition, the airborne lead emission rates from cars, expressed in grams of lead per mile, have been calculated from the lead collected on the filter. These data provide a means for direct comparison of the emission rate of airborne lead from cars operated on the road to the emission rates of lead from cars operated on the PCD. Such data, shown in Tables 1, 6, 7, and 9, were calculated from a knowledge of effective tunnel volume, volume of air filtered, sampling time, mean car speed, initial air lead concentration, and mass of lead on the filter.

LEAD EMISSIONS FROM PRODUCTION VEHICLES

The lead emission rates of several production vehicles have been measured and the data are summarized in Table 1. The emissions are expressed in terms of total emission rate of lead as measured by the total exhaust filter while the cars were driven on the PCD and airborne emission rate as measured in the Pennsylvania turnpike tunnel. The average total lead emission rate is approximately 0.11 gram of lead per mile. The airborne lead emission rate was 0.050 gram of lead per mile or less than half the total amount emitted. As will be shown later (Figures 7 and 8) the lead emission rate of a production vehicle is quite variable even over relatively long sampling periods of up to several hundred miles. The values shown for the emission rates in Table 1 are

TABLE 1 LEAD EMISSION RATE FROM PRODUCTION VEHICLES

Vehicle	Mileage	Emission rate, grams of lead per mile	
		Total	Airborne
F-47	0 to 54,000	0.086	
C-76	0 to 55,000	0.106	
C-82	8,000		0.039
H-1	41,000		0.061
CW-1	21,000		0.047
CW-21	11,000		0.055
C-40	0 to 28,000	0.102	
C-83	21,000	0.14	
	Average	0.108	0.050

the average results of at least three runs at the indicated mileages. In view of the variability in emission rates at different mileages on a given car and the variability among cars it is not possible to measure the amount of lead emitted from a production vehicle at any one time and expect to obtain a representative value of the lead emission rate of vehicles. Conversely, as is shown also in Figures 7 and 8, the lead emission rate of a vehicle equipped with a trapping system is relatively constant and the variations are much less than that for the standard vehicle. As a consequence, in all subsequent comparisons of the lead emission rates for the trap cars with that of standard cars the measured value of a given trap car will be compared with the average values for production vehicles as given in Table 1.

The size distributions of the lead emitted from three of the production vehicles listed in Table 1 have been determined at several points during mileage accumulation on these vehicles using the Federal mileage accumulation schedule (6). These data are summarized in Table 2. The total amount of lead emitted from the vehicles during the size measurements averaged just less than 0.1 gram per mile which is a quite close check on the total value given in Table 1. The emitted lead associated with particles greater than nine microns in equivalent diameter averaged 0.031 gram per mile or approximately 30 percent of the total amount of lead emitted. This material is relatively coarse and would not be expected to remain airborne for any significant length of time. Approximately 0.02 gram of lead per mile was emitted in the size range from nine to one microns equivalent diameters; particles of this size range might remain in the atmosphere for at least a short length of time. The rate of lead emission of particles of less than one micron in diameter was equal to 0.031 gram per mile or about 30 percent of the total lead emitted. These small particles would become airborne and remain suspended for a significant length of time. A further breakdown of the submicron lead particles shows that approximately 0.022 gram of lead per mile or about 20 percent is emitted as particles below 0.3 micron equivalent diameter.

In the same manner that the total lead emission rate varies with mileage, the amount of lead emitted in various size fractions also varies. However, the variation in emission rate is more pronounced for the large particles, i.e., those greater than nine microns. This variability is to be expected since the large particles are the result of re-entrainment of material which flakes off the walls of the exhaust system. The amount of material available for re-entrainment and the extent of flaking is dependent upon previous driving history of the car as well as the mode of car operation or the driving cycle used during the emission test. Thus, with relatively new cars, there will be little or no material available for re-entrainment in the exhaust system giving rise to very low emission rate of large particles. Similarly, under steady-state driving conditions there is little thermal expansion and contraction of the exhaust system and flaking and subsequent re-entrainment is minimal.

The smaller lead particles are combustion generated and thus the absolute lead emission rate is relatively constant as long as the test cycle or driving condition remains the same. However, due to the wide fluctuations of the emission rate of large particles, the relative amount of the small particles compared with the total amount emitted will fluctuate also. For example, measurements made with relatively low mileage vehicles or measurements made under steady-state test conditions, where the emission rate of large particles

TABLE 2 LEAD PARTICLE SIZE DISTRIBUTION FROM PRODUCTION VEHICLES

Vehicle	Mileage	Emission rates, grams of lead per mile				
			Size in microns			
		Total	>9	9 to 1	<1	<0.3
C-40	5,000	0.102	0.028	0.029	0.046	0.031
C-40	16,000	0.095	0.037	0.024	0.034	0.024
C-40	21,000	0.083	0.036	0.017	0.030	0.022
C-40	28,000	0.115	0.066	0.028	0.022	0.013
F-47	3,000		0.008	0.008	0.022	0.019
F-47	20,000	0.086	0.027	0.010	0.020	0.015
F-47	55,000		0.024	0.008	0.017	0.015
C-76	3,000		0.015	0.023	0.044	0.031
C-76	20,000	0.106	0.056	0.022	0.044	0.028
C-76	55,000		0.017	0.008	0.027	0.022
	Average	0.098	0.031	0.018	0.031	0.022

would be very low, will lead to the erroneous conclusion that most of the lead is omitted from the car as very fine particles. These observations undoubtedly explain why some investigators have reported that the majority of the lead is emitted as submicron particles.

ATMOSPHERIC LEAD PARTICLE SIZE

To place the size of the lead emitted from production vehicles in proper perspective, it is worthwhile to examine the particle size distribution of the lead in the atmosphere in various urban areas. Many investigators have made such measurements and their data are summarized in Table 3 (7, 8, 9). The most comprehensive work was carried out by Robinson and Ludwig who sampled the atmosphere in 59 urban areas and found that the average size or mass median equivalent diameter of the particles which contain lead was 0.25 micron in diameter. This means that one-half of all the lead by weight was associated with particles of greater than 0.25 micron in diameter and one-half of the lead by weight in the air was associated with particles of less than 0.25 micron in diameter. Other investigators have also measured average size of lead-containing particles in the atmosphere and in general their values are reasonably in agreement with those of Robinson and Ludwig. Habibi and Pierrard of duPont also measured the size distribution of atmospheric lead at two widely separated locations and as shown in Table 3 found the average particle size to be approximately 0.25 micron. Thus, an average particle size for the lead-containing particulate matter in the atmosphere would appear to be 0.25 micron mass median equivalent diameter.

When the lead particle size distribution emitted from production vehicles, as given in Table 2, is examined in terms of the size of the lead particles in the atmosphere, it can be seen that about 20 percent of the lead emitted from production vehicles consists of particles smaller than the average size of the lead particles found in the urban atmosphere. Thus, for a trapping system to be effective in reducing the amount of lead in the urban atmosphere it must reduce the total amount of lead emitted from a vehicle. But, it must also be effective in reducing the airborne lead which includes the lead emitted as particles smaller than one micron and, in particular, the particles smaller than 0.25 micron equivalent diameter.

LEAD EMISSIONS FROM TRAP-EQUIPPED VEHICLES

A number of different studies have been conducted at duPont to determine the best way to reduce the lead particulate exhaust emissions from cars operated on commercial gasolines. These studies have included electrostatic precipitation, changes in the chemical composition of the particulate lead, as well as chemical and mechanical filtration. However, the most durable and effective way to attain this reduction is to separate the particles from the gas stream and then retain or trap the particulate matter in the exhaust system using inertial separation devices.

Several such exhaust particulate trapping systems have been devised and described previously (2). One of these systems designated Trap System A, consists of the substitution of fluted pipes in place of the standard exhaust pipes and the use of a cyclone trap. The fluted pipes increased the heat transfer from the exhaust gas to the ambient air and provided the additional cooling necessary to initiate particulate lead formation in the

TABLE 3 SIZE OF ATMOSPHERIC LEAD PARTICLES

Investigator	Location sampled	Average size (mass median equivalent diameter), microns
Robinson and Ludwig	59 urban areas	0.25
Lee, Robinson and Wagman	Downtown Cincinnati	0.2
	Suburban Cincinnati	0.4
Lundgren	Riverside, California	0.5
Habibi	Wilmington, Delaware	0.24
Pierrard	El Monte, California	0.2
Weighted Average		0.25

exhaust system. The particles of lead which were formed in the fluted exhaust pipe were removed from the exhaust stream in simple cyclone traps and the lead particles stored in the cyclone trap collection chamber. This trap system was operated for 64,000 miles on the PCD using the Federal mileage accumulation schedule and a commercial gasoline containing 2.5 grams of lead per gallon. When the lead emission rates from this vehicle, as determined by the total exhaust filter, were compared with those of a production car it was found that the trapping system reduced the total lead emissions by 70 percent.

Trap System B

A more advanced particulate trap system designated Trap System B was devised to provide additional cooling and agglomeration. A schematic diagram of this trap system is shown in Figure 4. A dual exhaust system was used. On each side of the dual system two pipes were lined internally with wire mesh to promote agglomeration of the particles. In addition, the dual pipes exhausted into a common box filled with fine wire mesh. The gases flowed from this mesh box to two cyclone particle separators, one in each of the rear fender wells. The design of the cyclone separation box is shown in Figure 5. A photograph of the under side of the car with the Trap System B installed is shown in Figure 6.

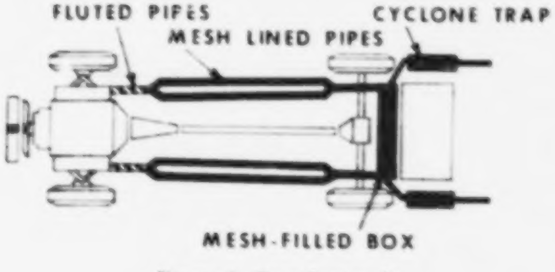

Figure 4. Trap System B

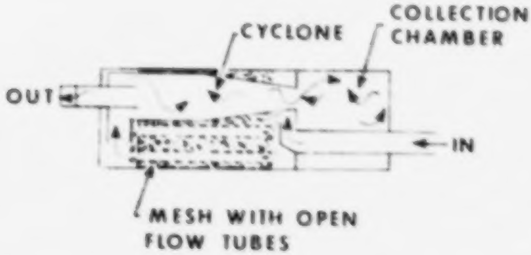

Figure 5. Cyclone separator for exhaust particulate matter.

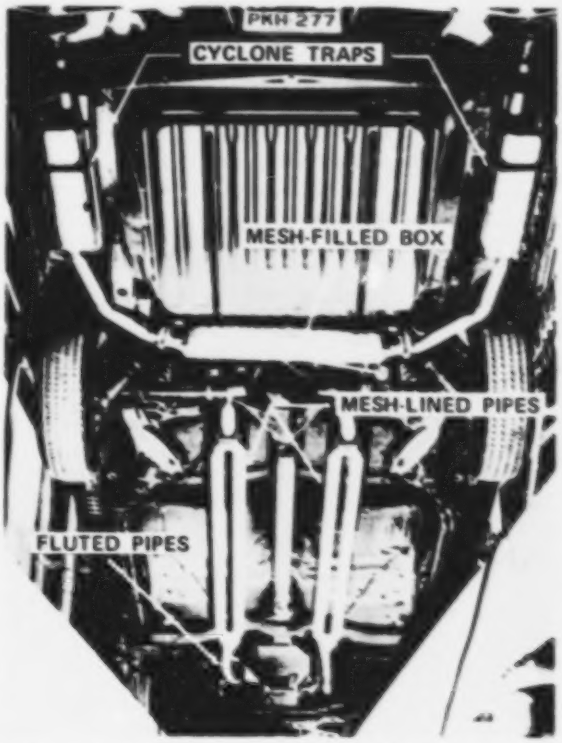

Figure 6. Exhaust particulate matter Trap System B.

The performance of the Trap System B was evaluated in a four-car test in which two 1969 Fords and two 1969 Chevrolets were used. One car of each make was equipped with the trap system and their performance in terms of lead emission rates compared with the production cars which retained the unmodified conventional exhaust systems. Mileage was accumulated on the PCD using the Federal mileage accumulation schedule. Commercial gasoline containing 2.5 grams of lead per gallon was used for all mileage accumulation and emission test work.

The total amount of lead emitted from all four vehicles was monitored continuously throughout the test, which lasted almost 60,000 miles, by the use of total exhaust filters. The results in terms of grams of lead emitted per mile of operation as a function of test miles are shown in Figures 7 and 8 for the production vehicles and for the vehicles equipped with Trap System B. As previously discussed, it is obvious that the lead emission rates from the production vehicles are quite variable with time and that the lead emission rate measured at any instant of time in the life history of an automobile may not be representative of the average amount of lead emitted over its lifetime. Conversely, the trap system was quite effective in reducing the amount of lead emitted and also in reducing the variations in the amount of lead emitted. The average amounts of lead emitted from the production vehicles and the vehicles equipped with Trap System B throughout the 60,000

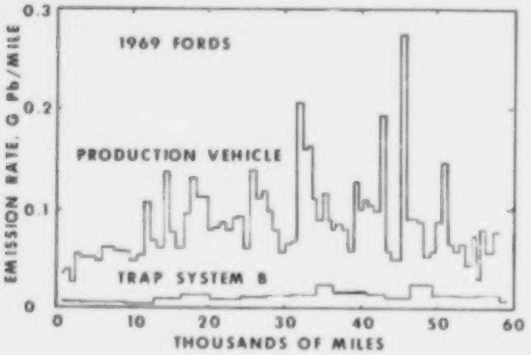

Figure 7. Lead emission rates for 1969 Fords with and without Trap System B.

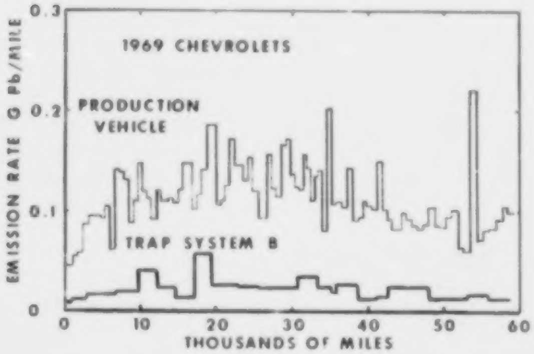

Figure 8. Lead emission rates for 1969 Chevrolets with and without Trap System B.

test miles are shown in Figure 9.

In addition to measuring the total lead emission rates, the particle size distribution of the emitted lead was determined in the 40-foot tunnel. The data for the two cars equipped with Trap System B are shown in Table 4.

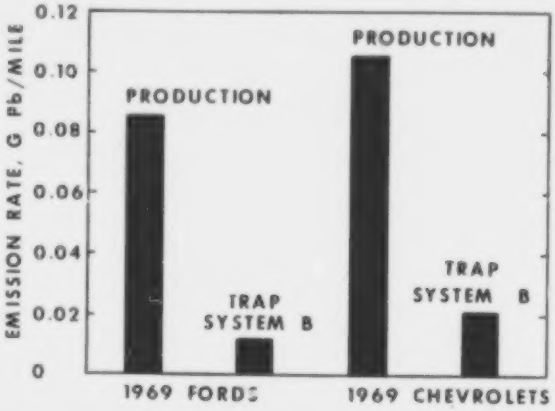

Figure 9. Average lead emission rates with and without Trap System B.

These data along with similar data obtained with the production vehicles are shown in Figure 10. The reduction in lead emission rate achieved with Trap System B when compared with the lead emission rates from production vehicles is summarized in Table 5.

Trap System B was most effective in reducing lead emission rates of both the large and the small particles. Trap System B reduced the total amount of lead emitted from production vehicles by some 82 percent. Examination of the size distribution of the emitted lead reveals that, as expected, the trapping system was particularly effective in reducing the large particles. The lead particles with sizes greater than nine microns were reduced by 94 percent. Even in the case of the smaller size fractions, significant reductions in emission rates were accomplished. There was an 88 percent reduction of the amount of particles emitted in the size fraction from nine to one microns and a 65 to 71 percent reduction in mass of particles of less than one micron diameter. This reduction in emission of the small

TABLE 4 LEAD PARTICLE SIZE DISTRIBUTION FROM PRODUCTION VEHICLES WITH TRAP SYSTEM B

Vehicle	Mileage	Emission rates, grams of lead per mile				
			Size in Microns			
		Total	>9	9 to 1	<1	<0.3
F-48	3,000		0.0004	0.0005	0.005	0.004
F-48	20,000	0.012	0.003	0.003	0.012	0.005
F-48	55,000		–	–	–	–
C-77	3,000		0.0005	0.0006	0.007	0.005
C-77	20,000	0.022	0.004	0.005	0.020	0.010
C-77	55,000		0.001	0.002	0.011	0.008
	Average	0.017	0.002	0.002	0.011	0.006

TABLE 5 LEAD EMISSION REDUCTION WITH TRAP SYSTEM B

Vehicle	Mileage	Reduction from production vehicle, %*				
		Size in microns				
		Total	>9	9 to 1	<1	<0.3
F-48	3,000		97	97	84	82
F-48	20,000	86	91	83	61	77
F-48	55,000		—	—	—	—
C-77	3,000		97	97	78	77
C-77	20,000	79	87	72	36	55
C-77	55,000		97	89	65	64
	Average	82	94	88	65	71

*See Tables 1, 2, and 4 for lead emission rates.

particles is most important since these are the particles which will tend to remain airborne and which correspond in size to the particles containing lead found in the atmosphere of urban areas.

The foregoing results obtained with Trap System B demonstrate that it is feasible to control the emission of particulate lead matter from vehicles. Furthermore, not only is the total amount of lead emitted from the vehicle reduced substantially, but the fine particles which could be expected to remain airborne for significant lengths of time are reduced also. However, this trapping system is somewhat complex. Accordingly, simpler systems have been devised in an attempt to reduce the cost and the complexity of the system while retaining or improving the high efficiency demonstrated with Trap System B.

Trap System C

A simpler version of Trap System B was devised and has been designated Trap System C. This system, shown schematically in Figure 11, consists of dual, fluted pipes which serve to cool the exhaust gases and initiate formation of the lead particulate matter. The gas flows from the fluted pipes into a common box filled with stainless steel wire mesh and through dual cyclone collection traps similar to the units used in Trap System B.

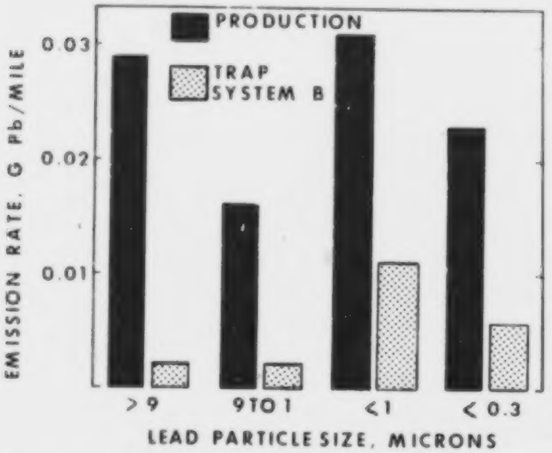

Figure 10. Lead emission rates from Trap System B as a function of particle size.

The effectiveness of Trap System C was determined by measuring the airborne lead emission rate of production vehicles before and after the installation of the trap system. Two vehicles, C-82 and H-1, were tested in the Pennsylvania turnpike tunnel as production vehicles. At the conclusion of these tests the production exhaust system was removed and Trap System C was installed. The trapping systems which were installed had already accumulated about 17,000 miles of consumer operation in a field service test using commercial leaded gasolines (10). After the traps were installed on the two vehicles the cars were operated in excess of 2,000 miles on the PCD to recondition the systems prior to the tests at the Pennsylvania turnpike tunnel. In the case of C-94, the car had been operated as a duPont total emission control system vehicle for 10,500 miles (see Ref. 10 and the

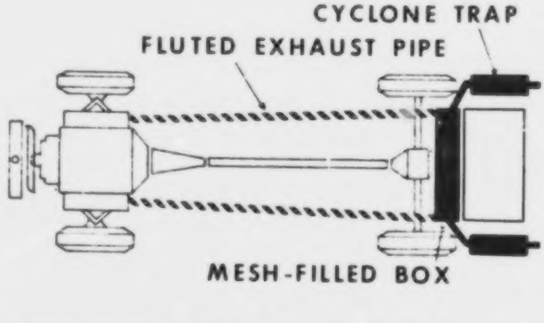

Figure 11. Exhaust particulate matter Trap System C.

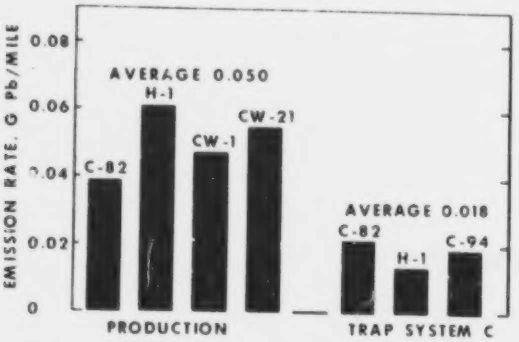

Figure 12. Airborne lead emission rates with Trap System C.

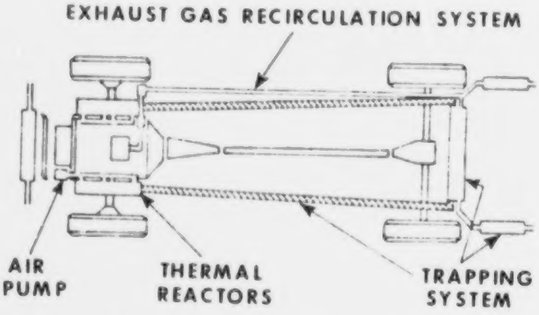

Figure 13. duPont total emission control system.

next section for description of these vehicles). To test the trap system only, the gaseous emission control system consisting of thermal reactors and exhaust gas recirculation systems was removed, the car restored to a production vehicle except for the Trap System C, the vehicle operated for another 2,000 miles, and then tested in the Pennsylvania turnpike tunnel to determine airborne lead emission rates.

The data obtained with the vehicles equipped with Trap System C are shown in Table 6 and are compared with the airborne emission rates of production vehicles in Figure 12. Trap System C was effective in reducing airborne emission rates to an average value of 0.018 gram of lead per mile. When this value is compared with the airborne lead emission rate of production vehicles it can be seen that Trap System C reduced the amount of airborne lead emitted by 64 percent.

duPont Total Emission Control System Vehicles

Trap System C has been combined with other systems to control the gaseous exhaust emissions from vehicles to produce a total emission control system or TECS I vehicle (10). The components of the TECS vehicle are shown schematically in Figure 13. The exhaust manifold thermal reactors are used in conjunction with an air pump to provide a high temperature zone where the hydrocarbons and carbon monoxide in the exhaust are oxidized. An exhaust gas recirculation system is combined with various carburetor modifications to control the emission of oxides of nitrogen. A more complete description of these vehicles and their performance in controlling gaseous emissions can be found in References (2, 10, and 11). Trap System C as utilized in these TECS vehicles is shown in the photograph in Figure 14.

The lead emission rates from several of the duPont TECS vehicles have been measured and the data summarized in Table 7. The average total lead emission rate for these vehicles was 0.016 gram per mile. When this value is compared with the value of the 0.108 gram per mile for production vehicles it can be seen that the TECS vehicles reduced the total amount of lead emitted to the environment by 85 percent. The amount of airborne lead emitted by the TECS vehicles as measured in the Pennsylvania turnpike tunnel averaged 0.015 gram per mile corresponding to a reduction of 70 percent as compared with the airborne emission rates of production vehicles.

TABLE 6 LEAD EMISSION RATE FROM PRODUCTION VEHICLES WITH TRAP SYSTEM C

Vehicle	Mileage	Airborne lead emission rate, grams of lead per mile	Reduction in airborne lead emission rate compared to production vehicles, %*
C-82	20,000	0.022	56
H-1	20,000	0.014	72
C-94	13,000	0.019	62
	Average	0.018	64

*See Table 1 for airborne lead emission rate for production vehicles.

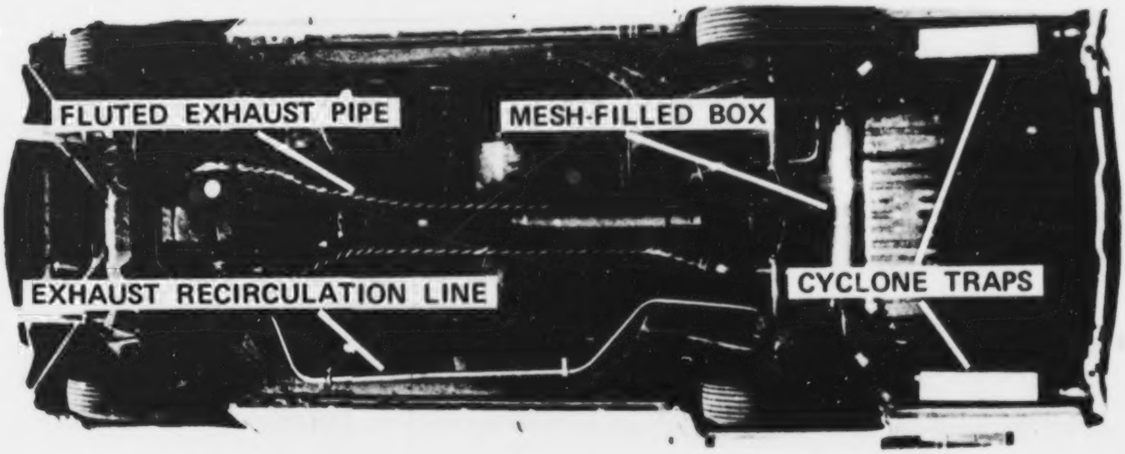

Figure 14. Trap System C as a part of the duPont TECS.

Muffler Lead Traps

The trapping systems as typified by Systems B and C are quite effective in reducing the emission of particulate lead from vehicles but they are complex and would probably be suitable only for installation on new vehicles at time of manufacture. In an effort to reduce the complexity and therefore the cost of the system and also to develop systems which might be used as replacement items for mufflers on existing cars on the road, a program to develop a lead trap the size and shape of a production muffler was initiated. The basis of the muffler lead trap is the use of a more efficient agglomerating medium than the stainless steel wire mesh. One method of improving the agglomeration of lead particles is to utilize a material with high surface area which has an affinity for the lead compounds in the exhaust. Such a material is high surface area alumina that has been used for a support in catalytic reactors. Accordingly, traps incorporating high surface area alumina in combination with cyclone separators have been built and tested.

TABLE 7 LEAD EMISSION RATE FROM DUPONT TECS VEHICLES

Vehicle	Mileage	Emission rate, grams of lead per mile	
		Total	Airborne
C-84	1,000	0.021	
C-85	9,400	0.011	
C-86	26,000	0.015	
C-86	30,000		0.009
C-94	10,500		0.022
	Average	0.016	0.015
Reduction in lead emission rate compared with production vehicles, percent (see Table 1 for production vehicles)		85	70

A muffler lead trap, designated Type II, incorporated extended surface alumina in the form of one-quarter inch diameter pellets and two cyclone separators in parallel. The design of this trap is shown in Figure 15. This trap is the same overall size and shape as a production muffler. Exhaust gas enters one end of the trap, flows through the bed of alumina pellets, and into the two cyclones. After exiting from the cyclones the exhaust flows into a plenum chamber at the downstream end of the trap. This trap was installed in place of the standard muffler on a production vehicle and was operated on the PCD under the Federal mileage accumulation schedule for 25,000 miles. During this time the lead emission rate was monitored and the values obtained are shown in Table 8.

The average total lead emission rate obtained with this trap was 0.011 gram of lead per mile or a 90 percent reduction when compared with a production vehicle. After about 20,000 miles, it was observed that

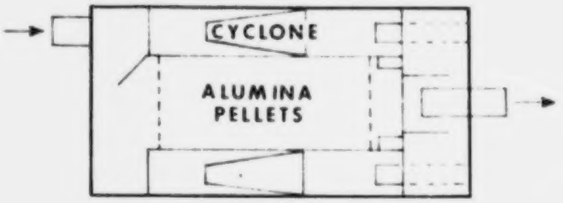

Figure 15. Muffler lead trap type II.

TABLE 8 LEAD EMISSION RATE FROM PRODUCTION VEHICLE WITH MUFFLER LEAD TRAP TYPE II

Vehicle C-83

Mileage	Emission rate, grams of lead per mile	
	Total	Airborne
0		
6,000	0.012	
9,000	0.014	
12,000	0.009	
15,000	0.008	
18,000	0.006	
21,000	0.016	
25,000	0.014	0.021*
Average	0.011	0.021*
Reduction in lead emissions compared with production vehicles, percent (see Table 1 for production vehicles)	90	58*

*Trap filled to capacity with collected lead salts.

particulate lead was being emitted in relatively large quantities from the tail pipe of the vehicle during high speed operation. Investigations revealed that the cyclone collection chambers had become totally filled with the collected lead salts and that this material was being re-entrained in the exhaust. An attempt was made to clean out some of the material in the collection chambers and the vehicle was then taken to the Pennsylvania turnpike tunnel for determination of airborne lead emission rates. The tests in the turnpike tunnel showed an airborne emission rate of 0.021 gram per mile or a 58 percent reduction from the production vehicles. This relatively poor showing in terms of airborne lead emission rate was due to the fact that significant quantities of lead were still being re-entrained from the particle collection chambers and the trap was simply too full of lead to be fully effective in reducing the amount of lead emitted from the vehicle.

The Type II trap was disassembled after 25,000 miles of operation. The alumina pellets were undamaged and showed no signs of any attrition. The material accumulated in the cyclone collection chambers was analyzed and found to contain only trace amounts of alumina confirming that very little attrition of the pellets had occurred.

To overcome the problem of re-entrainment of the collected lead material which had occurred with the Type II trap another muffler lead trap, designated Type III, was built. This trap is shown in Figure 16. It was of the same overall size and shape as the Type II trap but the internal components had been rearranged to increase the volume of the particle collection chamber. The flow path was quite similar to that of the Type II trap; the exhaust gases flowed first through the bed of alumina pellets then in parallel through the cyclones and exited from the plenum chamber. This trap was installed in place of the production muffler on a vehicle and is currently under test. Four thousand miles have been accumulated on the PCD using the Federal mileage accumulation schedule. The lead emission rate from the vehicle as determined to date is shown in Table 9.

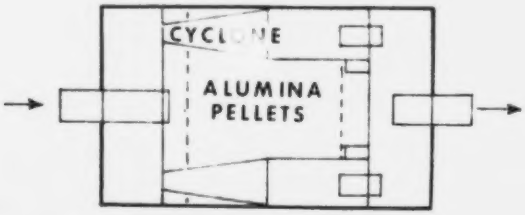

Figure 16. Muffler lead trap type III.

The total amount of lead emitted as measured by the total filter averaged 0.010 gram of lead per mile and compared with the production vehicle the Type III trap has reduced the total amount of lead by 91 percent. This vehicle has been tested at the Pennsylvania turnpike tunnel to determine the airborne lead emission rate and the value was found to be 0.008 gram of airborne lead per mile. When this value is compared with the production vehicles it can be seen that the Type III trap reduced the airborne lead emission rate by 84 percent.

These preliminary results on the Type III muffler lead trap are most encouraging. The trap has been designed to have sufficient collection capacity to hold all the lead salts emitted from the vehicle for at least 50,000 miles.

TABLE 9 LEAD EMISSION RATE FROM PRODUCTION VEHICLE WITH MUFFLER LEAD TRAP TYPE III

Vehicle C-82

Mileage	Emission rate, grams of lead per mile	
	Total	Airborne
2,000	0.009	
4,000	0.010	0.008
Average	0.010	0.008
Reduction in lead emission rate compared with production vehicles, percent (see Table 1 for production vehicles)	91	84

Further testing of this trap is planned to determine the reduction in lead emissions over extended mileage and to determine the ultimate effective life of the trap.

EFFECT OF TRAP SYSTEMS ON ATMOSPHERIC LEAD LEVELS

From the foregoing discussion it is obvious that the various trapping systems investigated are quite effective in reducing the amount of lead emitted from the tail pipe of vehicles. However, the important question that must be resolved is whether this reduction in lead emissions from the tail pipe will translate into a similar reduction in the amount of lead contained in the atmosphere. Direct measurements are available to answer this question and to demonstrate the effectiveness of the trapping systems. The amounts of lead collected from the air in the Pennsylvania turnpike tunnel after driving various vehicles on the road in the tunnel were measured and the results of these measurements are summarized in Table 10.

Four different vehicles with production exhaust systems were run for a total of 13 tests in the Pennsylvania turnpike tunnel. The air in the tunnel was sampled, as described earlier, and the average amount of lead collected on the sampling filter was found to be 101 micrograms. Similarly, three different vehicles equipped with Trap System C were run for a total of ten tests in the tunnel. The average amount of lead collected from the air in the tunnel after running the cars with Trap System C was 37 micrograms. Comparison of these two numbers shows that Trap System C reduced the amount of lead in the air by 64 percent.

Two other vehicles equipped with the duPont total emission control system, which consists of thermal reactor and exhaust gas recirculation systems and which includes Trap System C, were run in the Pennsylvania turnpike tunnel for a total of six tests. The average airborne lead collected from the air in the tunnel after running these vehicles was 29 micrograms and comparison of this number to that obtained with the production vehicles shows that the reduction in airborne lead caused by the installation of the total emission control system was 71 percent.

One vehicle equipped with muffler lead trap Type III was run in the tunnel for a total of three tests and the average amount of airborne lead collected on the sampling filter was found to be 16 micrograms. Once again, comparison of this value to the value of 101 micrograms for the production vehicles showed the reduction of airborne lead caused by the installation of the Type III muffler lead trap was 84 percent.

It is clear that not only do these trap systems bring about significant reductions in the total amount of lead emitted from the tail pipe of vehicles but they are most effective also in reducing the actual amount of lead remaining in the air after cars have been driven on the road in a representative consumer-type driving cycle.

CONCLUSIONS

- Vehicle exhaust particulate lead traps are effective in reducing the total amount of lead emitted from production vehicles operated on commercial leaded gasoline by 82 to 91 percent as measured by laboratory tests.
- Laboratory size-measurement of the emitted lead particles showed that the traps not only reduced the large size particles by better than 90 percent, but also reduced the particles smaller than 0.3 micron (or particles which are in the same size range as those found in urban atmosphere) by 71 percent.
- These same lead traps reduced the amount of emitted airborne lead particles by 64 to 84 percent when measured in road tests in a vehicular turnpike tunnel.
- Vehicles equipped with lead traps for particulate control and a gaseous emission control system consisting of thermal manifold reactor and exhaust gas

TABLE 10 REDUCTION OF AIRBORNE LEAD IN THE PENNSYLVANIA TURNPIKE TUNNEL DUE TO THE USE OF TRAP SYSTEMS

Exhaust systems	No. of cars	No. of tests	Average* airborne lead collected on filter, μg	Reduction in airborne lead, %
Production	4	13	101	
Trap System C	3	10	37	64
duPont total emission control system (Trap System C)	2	6	29	71
Muffler lead trap type III	1	3	16	84

*Corrected for differences in total volume of air sampled and ambient air lead levels.

recirculation systems, reduced total lead emitted by 85 percent and lead in the air in the vehicular tunnel was reduced by 71 percent when compared with production vehicles.

Compact, effective lead traps which incorporate alumina pellets and cyclone collectors have been developed which are suitable for replacement of mufflers on existing cars now on the road.

These lead traps are relatively simple and have no moving parts. Based on the reported tests, they do not deteriorate in effectiveness with mileage, require no maintenance, and should last the life of the vehicle.

ACKNOWLEDGMENTS

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TRACE ELEMENT EMISSIONS FROM THE COMBUSTION OF FOSSIL FUELS

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THE CONCERNS AND THEIR ORIGINS

Over the last several years there has been a growing interest in the redistribution, driven or aided by human actions, of certain elements which are ordinarily referred to as trace elements. The meaning of the term itself varies conspicuously with the investigator; that being the case, it seems appropriate that this paper contain at the outset a specification of what is meant by that term when used here. I have taken the liberty of defining trace elements to exclude:

1. All of the elements which are gasses at ordinary temperatures and pressures;
2. Nearly all of the elements of generally high crustal abundance, such as sodium, potassium, magnesium, aluminum, calcium, phosphorus, sulfur, silicon, and iron. Arguments can be advanced for retaining some of these in the trace elements category, example, because some are trace in a dietary sense, or simply because their emissions from a particular class of sources are generally small. However, these ubiquitous contaminants confront humans and their activities in such a welter of ways that it is unlikely that any particular human activity plays a dominant role in that exposure;
3. Specific compounds or minerals, such as asbestos. It is fully recognized, however, that no assessment of the impact of any trace element should be made without knowledge as to the form in which such element is manifested; the wide variation in toxicity among the mercurials, and in particular the recent emergence of methyl mercury as a major toxic agent, are object lessons; and, finally,
4. Those elements for which the principal toxic effects are a result of their radioactive nature. This last exclusion is made simply in the name of limiting the subject matter of this paper; I am in no way denying that such emissions exist nor that there may be reasonable concern over their effects.

Proceeding, then, from such an exclusionary definition to the circumstances which have focussed attention on the remaining trace elements, we find three major forces have been at work:

1. Multivariate epidemiological studies have occasionally yielded positive correlations between clinical effects and atmospheric levels of one or more trace elements; whether by chance, by joint association, or from genuine cause-effect relationships. Coupled with this, an increased interest has developed in the nutritional value of various trace elements.
2. Researchers in toxicology, concerned, perhaps justly, over the lack of toxicological corroboration of the presumed long-term, low-level effects of major air contaminants such as sulfur dioxide, have quite naturally returned to examination of known toxicants, especially the heavy metals.
3. A ground swell of public arousal, some of it probably carried over from frank poisoning cases involving either water-borne contamination or ingestion of lead-based paints, has resulted in regulatory activity and interest, especially as regards mercury and lead. Whether or not such action is well-advised, it has resulted in attempts at emission inventories which go well beyond those contaminants which have been the usual objects of suspicion.

The present focus on trace element emissions is at once the result of direct scientific experiment; of scientific hunchmanship (which I do not derogate); and of at least a modicum of public hue and cry, whether for better or worse.

SOURCES OF TRACE ELEMENTS IN COMBUSTION SYSTEMS

As indicated earlier, this paper is concerned with a class of emission sources – combustion sources utilizing fossil fuels – and carries a special emphasis on large sources such as electric utility furnaces. The origins for the trace elements emitted by such sources are obviously to be found chiefly in their fuels. Moreover, of the three

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TABLE 1 TRACE ELEMENTS IN OILS

Element	Concentration – ppm
Beryllium	.0004
Boron	.002
Scandium	.001
Titanium	.1
Vanadium	50.
Chromium	.3
Manganese	.1
Cobalt	.2
Nickel	10.
Copper	.14
Zinc	.25
Gallium	.01
Germanium	.001
Arsenic	.01
Selenium	.17
Strontium	.1
Yttrium	.001
Molybdenum	10.
Cadmium	.01
Tin	.01
Barium	.1
Mercury	10.
Lead	.3

Note: These data sometimes represent only a single field, and therefore may be either anomalously high or low.

chief fossil fuel resources, one, natural gas, appears to have no consequential content of trace elements. I hasten to add that natural gas is in increasingly short supply, most especially as a utility fuel, so that its desirable characteristics are essentially unavailable for control purposes. Our discussion must therefore continue to examine the remaining fuels, namely, petroleum fractions and coal.

Oils

Most utility fuels, like the fuels used for space heating in small-to-medium-sized residential, commercial, and industrial furnaces, fall into the classifications of distillate oils, grade numbers 1 and 2, and residual oils, grade numbers 5 and 6. A limited amount of crude oil is also burned without refinement, and the future may see increased use of intermediate oils, about number 4, or blends, and perhaps of some fractions beyond residual, for example, tars or pitch. There are few published data concerning trace element contents of these various oil fractions. It is reasonable to conclude that the distillate oils are probably lower in most trace elements than their respective crudes, while residuals may well be higher. Table 1 gives the concentration ranges for various elements in oil in ppm, as listed by various authors. With the paucity of data available, it cannot be assumed that any of these figures are really representative of common fuels.

One factor which should not be overlooked in analyzing the impact of oil fuels is the addition of additives to improve combustion and/or ash collection. For example, particularly with high-vanadium oils, additives containing manganese are frequently incorporated in the fuel as a means of improving particulate emission control and stack appearance.

Coals

Coals are an almost classic mixture of many constituents. With respect to trace elements, there is simply no such animal as a representative coal, even for a universe as small as a single mine. Moreover, just as environmental pressures have forced many companies to essentially abandon coal fuel, only four generating stations in the East Coast region are not now committed

TABLE 2 TRACE ELEMENTS IN COALS

Element	Concentration–ppm
Beryllium	3
Boron	75
Scandium	5
Titanium	500
Vanadium	25
Chromium	10
Manganese	50
Cobalt	5
Nickel	15
Copper	15
Zinc	50
Gallium	7
Germanium	5
Arsenic	5
Selenium	3
Rubidium	100
Strontium	500
Yttrium	10
Molybdenum	5
Tin	2
Barium	500
Mercury	.01-.5
Lead	25

Note: These data represent only a few samples each, and therefore may be either anomalously high or low.

to oil fuel; many coal burning facilities have shifted, or contemplate a shift, to coals quite different than those intended in their design. The elemental content of these newer fuels has not been well established. The literature suggests the range of coal trace element concentrations which is shown in Table 2. It will be noted that not only are the concentrations quite different from those for oil fuel, but indeed a quite different set of elements predominate.

SINKS FOR TRACE ELEMENTS IN COMBUSTION SYSTEMS

The above data for oil and coal-fueled power generation consider only the initial content of trace elements in the fuels used. Before it can be ascertained what actual emissions to the atmosphere may result from use of these fuels, it is necessary to consider what other routes may be taken by an atom of a particular element. Figure 1 is a schematic diagram of a large generating unit. Neglecting deposition of trace elements upon, or their combination with, the surfaces of the boiler, ducts, or stack, there are still two possible exits for their release from the furnace. The first is collection with the slag, or molten fuel impurities; the second is passage into the ducts leading toward the stack. The possibility of significant attrition in the slag is very good, particularly for coal-fired furnaces; it is well established that of the ash normally present in coals, at least 20 percent and often as much as 80 percent, is retained as slag in modern furnaces. There is, therefore, a reasonable chance that trace elements will be entrained in, or will combine with, such a slag flow and will, therefore, be prevented from reaching an air emission site.

The remaining releases ordinarily face a second barrier before they may exit the plant. That barrier is in the form of pollution control equipment, a feature of most utility installations since the late 1920's. There are at least four types of pollution control equipment in use or under construction for utilities today: Mechanical collectors; electrostatic precipitators; baghouses; and scrubbers. All of these devices are aimed principally at reducing the emissions of particulates; therefore, they are generally effective if the material to be collected is in a condensed or combined form as it passes through the control equipment. Each type of control equipment has its own characteristics, which deserve some comment individually.

Mechanical Collectors

Mechanical collection, known also as cyclone or multiclone collection or under various other trade names, utilizes centrifugal separation of particles from the gas streams which carry them. The collection is obviously dependent upon the size and density of the

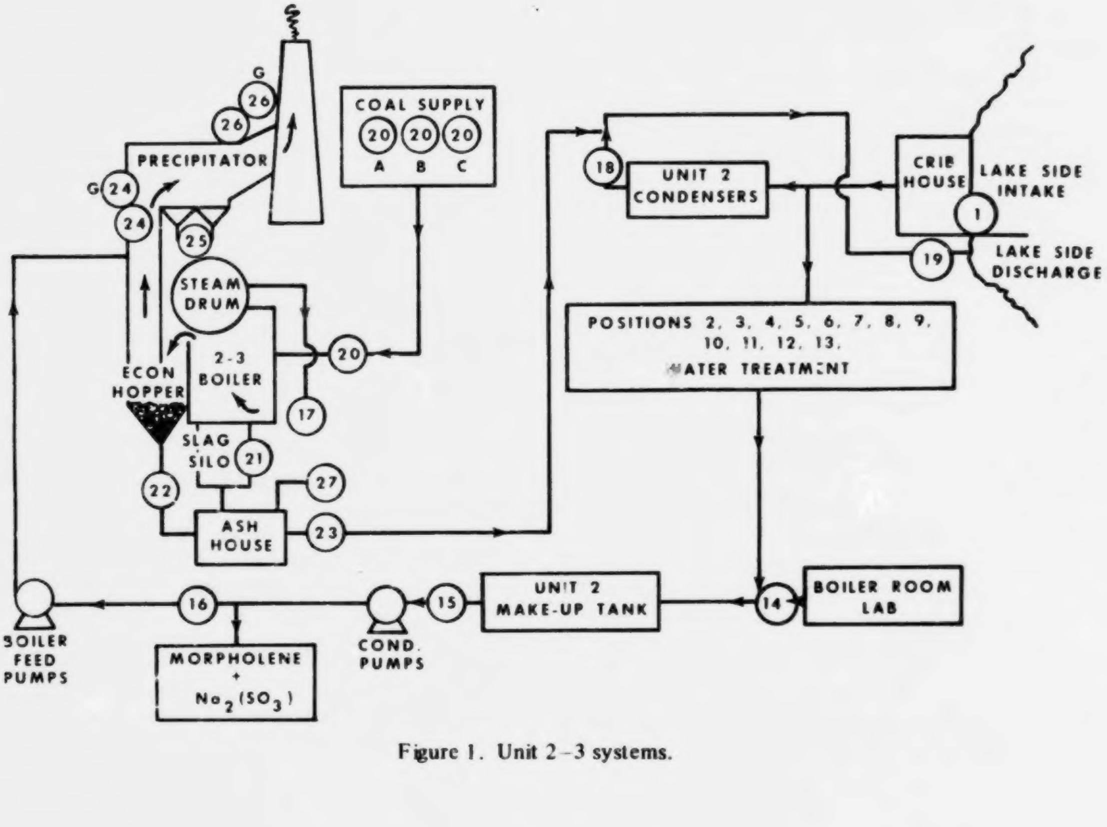
G
26
26
PRECIPITATOR
G
24
24
25
COAL SUPPLY
20 20 20
A B C
STEAM DRUM
ECON HOPPER
2-3 BOILER
20
17
SLAG SILO
21
22
27
ASH HOUSE
23
18
UNIT 2 CONDENSERS
CRIB HOUSE
LAKE SIDE INTAKE
1
19
LAKE SIDE DISCHARGE
POSITIONS 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13,
WATER TREATMENT
BOILER ROOM LAB
14
UNIT 2 MAKE-UP TANK
15
COND. PUMPS
16
BOILER FEED PUMPS
MORPHOLENE + $Na_2(SO_3)$

Figure 1. Unit 2–3 systems.

particles. Cyclones have been popular on small industrial-size boilers; for stoker firing, which produces a high fraction of large particulate; and for oil firing. Collection efficiencies in the range of 70 to 80 percent are readily achieved; higher efficiencies are often claimed and may be achieved on certain kinds of particulate, or where dust loadings at the control equipment inlet are extremely high. Changes in the type of fuel, even though the apparent fuel parameters do not change, may alter the collection pattern drastically; for example, it is reported that the Venezuelan-based residual oils are less satisfactory with such controls than the domestic and Middle Eastern oils.

Electrostatic Precipitators

These devices have been the technology of choice for many years on pulverized coal-fired and cyclone-fired boilers. Design efficiencies range from about 88 to beyond 99 percent. Some use of electrostatic collection has also occurred for both residual and distillate oils. In both mechanical and electrostatic precipitators the gas temperature in the control device is typically 250 to 350 F, although a new type of precipitator, the hot precipitator, has recently been introduced, which functions in ambient temperatures of 800 to 1000 F. It is ordinarily placed in the gas stream ahead of the air much more efficient for large particles, but we have not seen substantiation of that either in the literature nor in our own experience.

Baghouses

Bag filters have been used experimentally on oil-fired furnaces and one is now being constructed for a medium-sized coal-fired unit. Bag lifetime is a difficult operating problem. To my knowledge, no one has run tests on bag filter efficiency for these purposes; it is widely assumed to be very high. Gas temperatures must be held above the dew point to avoid acid attack.

Scrubbers

Some scrubbers have been built for particulate control on coal and oil-fired units. Recently there has been an upsurge in interest because of the potential for sulfur (and perhaps nitrogen) oxide removal. It has been hypothesized that scrubbers might also accumulate trace elements such as mercury. Again, that has not been established.

CASE STUDY: MERCURY

Of the trace elements, mercury has received, by far, the most attention. As a result of the obvious public interest in this contaminant, Commonwealth Edison engaged Swanson Environmental Consultants, Inc. of Farmington, Michigan, to do a mercury mass balance analysis on our State Line Generating Station in Hammond, Indiana.[2] This study was completed during January of 1971. As has been reported for other similar studies, it was not possible to achieve an accurate mass balance, probably due to the very low concentrations involved and the particularly difficult determination of the average level of mercury in the coal. Nonetheless, the results are somewhat illuminating, as shown in Table 3. Stated simply, our conclusions are as follow: Essentially all the mercury enters in the fuel itself; while some concentration takes place in slag and ash, the loss of mercury to these sinks is negligible, and apparently most of the mercury is emitted from the stack.

TABLE 3 GENERAL RESULTS OF MERCURY BALANCE ON A COAL-FIRED GENERATING STATION

Mercury input:	
Fuel	100 %
Air, water, etc.	Negligible
Mercury output in:	
Slag	4.5%
Precipitated ash	4.8%
Unprecipitated ash	.1%
Flue gas	78 %
Water, etc.	Negligible
	87.4%
Apparent error in balance	12.6%
	100 %

Analytical method for most measurements: Atomic Absorption.

I hasten to add that mercury may not be, probably is not, representative of other trace elements. For example, the boiling point of the elemental metal is 357 C or about 685 F; a temperature that is easily possible within the flue gas stream. Few other trace elements are in that range. Thus, metallic mercury might pass through electrostatic precipitators in vapor form, while any trace elements solidifying might be trapped by control equipment. This is merely hypothesis at present; but its application may have important consequences for future control strategies.

IMPACT OF FUEL COMBUSTION EMISSIONS

It would be easy, given the figures of my previous tables, to extend the calculations to the number of pounds of each element per day, per month, or per year emitted by any one source or combination of sources. Some authors have, in fact, done exactly that. Such an exercise yields heat without illumination; it is reprehensible for two reasons. The first, which I have already remarked, is the unknown chemical and physical form of these emissions; essential to any understanding of their biological significance. I must add that emissions from large combustion sources, such as power generating facilities, are apt to be strongly bound inorganic compounds, mixtures, and alloys. Organic compounds are quite unlikely outcomes of such oxidizing, high-temperature, low-carbon environments. Conversely, small-scale combustion of fuels, incineration, heating, and mobile sources may result in reactive and complex compounds.

Secondly, the lessons of air quality prediction learned on other battlefields include the pre-eminent role of micrometeorological factors: source stack height, gas flow, gas temperature, particle size, and atmospheric stability and wind parameters. The large sources may not, and probably do not, constitute the most important contributors to general ambient air quality. Failure to consider these factors may result in encouraging small, reactive, poorly distributed emission sources while penalizing large, controllable ones. I should not need to belabor that lesson; the consequences of not learning it could redound to the detriment of millions of people.

RESEARCH NEEDED AND IN PROGRESS

Obviously, one set of important facts not yet known is the behavior of trace elements in combustion systems. How much of element E is captured in the slag? How much in precipitated fly ash? In what chemical form does element E appear, oxide, sulfide, what? These questions, and related ones, are the subject of a project to begin shortly here at Batelle-Columbus under the sponsorship of the Edison Electric Institute; the trade association for the private electric utility industry.

Another set of data which is of interest concerns the transport and fate of trace element contaminants in urban atmospheres. New York University is studying this subject, under the sponsorship of Edison Electric Institute and the American Petroleum Institute. This study includes analysis of deposition in human lung tissue, as well as study of samples of suspended particulate from several New York City locations.

Finally, United States Environmental Protection Agency and various agencies around the county have programs in the works to determine the trace element content of a variety of fuels, so that more accurate assessmentof, at least, the fuel combustion input can be made.

CONCLUSIONS

A variety of kinds of data are thus accumulating toward knowledge of the movements of trace elements, with and without the assistance of man. The facts as of this date are these:

1. Trace element emissions from combustion systems cannot yet be readily quantified.
2. The effects of current levels of airborne trace elements on health and welfare are not yet known, but there is little reliable evidence of critical association and essentially none of causation.
3. Our mandate, therefore, is to seek knowledge about effects, mechanisms, emission sources, and controls, so that intelligent and objective decisions can be made. Emotion is to be eschewed: An attack on an unknown enemy may exact a dear price without commensurate gain.

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LUNCHEON ADDRESS

Martin Lang
Commissioner of Water Resources

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LUNCHEON ADDRESS

MARTIN LANG
Commissioner of Water Resources
City of New York, New York

As a career civil servant, I've spent some 30 years in the city. I admit that some of those years have been very odd; but you know, here in the heartland of America I have detected the presence of a kind of urbanphobia, or an irrational fear that is triggered whenever New York City is mentioned. Really, New York is no different from Columbus or Cincinnati or Chicago. It's just that in the pressure cooker of that city, things tend to happen sooner, and perhaps to a more intense degree, than anywhere else. Actually, what happens in New York is just a portent of things to come in all the other megalopolitan areas across the country. But today I'd like to point out that in one area at least – the area of water pollution control – I think that New York City stands ahead of all other coastal cities in the world, and ahead of many inland cities as well.

A statement like that may surprise many of you, but let me take a few moments to tell you a little about the Department of Water Resources and our commitment to impounding, protecting, and distributing to every citizen of the city (and to some of the surrounding counties, too) an ample supply of the best potable water in the world. I am charged with gathering up that slightly used water supply, conveying it away from the people's doorsteps, and treating and discharging it to the peripheral waters of the city in such a way as to keep it innocuous. Now that means that my department is responsible for the construction, operation, and maintenance of all water supply facilities. We are also in charge of the design, construction, operation, and maintenance of all water pollution control facilities (including the interceptors and a fleet of five ocean going sludge vessels); and the design, construction, and maintenance of all the sewers in the city. I have 6,000 miles of water mains (some of them well over 100 years old) and 6,000 miles of sewers. Sometimes I feel that each mile is draped like an albatross around my neck. But I feel fortunate to be in a city that as early as 1920 began to put their money where their convictions were. And I feel fortunate to be in a city where the present mayor is a real champion of the urban environment and has put his money where his convictions are in that respect.

In New York City there are various kinds of budgets. There is the capital budget, the expense budget, and the work performance budget. Then, following the Federal lead, we are trying to introduce something called the Program Planning Budget. The value of this system is that it makes you define what you're doing in terms of your actual mission. My mission in water pollution control is not specifically to treat sewage. No, my mission is to protect and enhance the marine environment; to protect and enhance the receiving waters. When you look at it that way, your attitude toward everything changes. To me, the important issue is no longer the development of technical minutiae that you can control. All our sophisticated techniques for removing metals – sulfide precipitation, reverse osmosis, electrophoresis, electrodialysis, etc. – are useless if we can't face up to the real issue of how to dispose of the end product. Now that I have this sludge, now that I've dried it, now that I have it as a hydroxide slurry, what do I do with it? That's a little tougher. I could go on at great length and tell you all about the activated sludge process and some of the innovations we have made in it. I could tell you all about mixed sludge thickening, interstage elutriation, high rate digestion, and all the various modifications of the activated sludge process in which my department has had some innovative input. But that would be evading the real issue, which is what happens in the receiving waters. The payoff in all our efforts is what actually happens in the environment. The environment doesn't know percentage removal. Every drop of water in our bay and harbors only knows its immediate microenvironment and the load on it. It knows nothing about percent BOD removal.

Until that day when we can take the wastes of mankind to where the tectonic plates override the ocean deeps and reincorporate them into the magma of the earth, we have only three options for waste disposal. The three ultimate dumps for everything are the air, the water, and the land. You all saw a chart this morning that neatly channeled waste in four directions. The end products in this case all got off the flow chart, but they are still part of the environment, and we must consider the total impact they will have on that environment.

I am a practicing ecologist and environmentalist, and I say that with all due modesty. You have attended many environmental conferences, and many of you have read about the fragile ecosystems of the tundra, the savannah, the rain forest, the estuary, and the desert. We are all concerned about the buildup of DDT in the body fat of the Antarctic penguin, the extinction of the blue whale, the necessity of preserving the California condor, and the fragility of the eggs of the peregrine falcon because of pesticide buildups. I believe in all that and I've worked to abate these blights on our environment. More particularly I am concerned about another fragile ecosystem – the urban ecosystem, where eight million agitated people are penned up in 300 square miles of land. I am charged with the two precious life support systems for this fragile urban ecosystem: the water supply and the used water supply.

In the area of ecology there are many self-appointed and self-anointed prophets of doom who say the sky is falling. Their favorite term is "irreversible damage." I am pleased now to give you some report on this with respect to New York City and to give you some supporting data for the statement I made earlier that New York stands ahead of all other coastal cities in the world in the area of water pollution control.

New York City is fortunate to have base line data on a harbor survey going back to 1909. It's too bad we don't have such similar data for all our waters. We don't know what the lead was along the highways in 1910 or what the mercury content of fish was. You know, environmental base line data are very important because they sometimes enable us to discern between long-term, natural, cyclical changes and manmade changes in the environment. But at least in our harbor we have that data and it shows the degradation of our estuary waters in the years between 1912 and 1917.

And then something happened in the City of New York that maligned city that always invokes a little snicker. The people of the City of New York started to put their money where their convictions were. In the 1920's the City began to build a series of secondary treatment plants – on salt water mind you, not on a potable water shed, not on inland fresh water, but on a tidal salt water estuary. And they did it during the depression. Interrupted by World War II, they plowed ahead. At present they are treating 1.1 billion gallons a day of our waste water supply by secondary treatment. We still have some raw discharges, but I have initiated a $1.5 billion program for the upgrading and expansion of all of our plants and the creation of two huge new super plants in the city, one of which (the North River Plant) is under construction today. The avowed intent is that by the end of this decade we will treat all the dry weather waste water flow of the City of New York to +90 percent BOD and suspended solids removal. Incidentally, New York City has addressed itself to what might seem to some of you a very quixotic enterprise (but I assure you that it is not). In the latter half of the 20th century we're going to restore bathing beaches already abandoned and create new bathing beaches in the heart of megalopolis in Jamaica Bay. I have the first such prototype plant on stream right now in Jamaica Bay, the Spring Creek Plant, which is designed to take care of the combined overflows that are a problem for many of the coastal cities.

Now with all this kind of activity, we're not complacent at all. The people of the city have a right to ask what we are getting for all our efforts. By that very sensitive parameter of dissolved oxygen (DO), New York City can show that today, in 1972, we have raised the dissolved oxygen level to a point not seen since the early years of this century. I repeat, we have dragged up the DO of all the major branches of the harbor to a level not seen since about 1910 or 1912. And we're doing that while carrying on our backs, so to speak, the discharge from our neighboring state, New Jersey.

Those of you who are familiar with New York can remember the best nickel's work in the city – a ride on the Staten Island Ferry. It was a cheap date to take a girl for a ride from the Battery to Staten Island along the upper bay there, to stand up on the bow and say "Oh, what salt spray." You were going through the dispersion field of the Passaic Valley, which disperses slightly less than 300 million gallons of sewage a day – sewage that is twice the strength of New York City sewage and not disinfected. But remember what I said: the marine environment only knows the load. It doesn't know percentage removal. It doesn't know what is being taken out; it only knows what is being added to it. Now that we can see this, there is some light on the horizon. And now that New Jersey is beginning to follow our example, I can assure you that our inshore estuarine waters will come to a level within the next decade and a half not seen in the memory of living man.

So, while all the prophets of disaster are just talking, some of the engineers are doing something about it. You know, you're not going to do anything to the environment with rhetoric. You're going to do it with plans, with engineering, and with hardware. You're going to do it with trained men and designs. Mere talk is not going to do anything; we've gone past the talking stage.

Now this brings me to metals. New York City's program was based on the digestion of sludge and the marine disposal of that sludge at the approved point offshore under permit approval of the Corps of Engineers. In 1957, I was the first organizer. I wrote the industrial waste regulations of the City of New York, and I saw them through until they became law and until we set up an industrial waste section (which has been growing ever since). This industrial waste control was divided into two parts. First, the city levied a surcharge to cover a proportionate share of the extra cost of treating approved wastes of high strengths. Second, certain wastes – toxic, dangerous, inflammable, explosive, or obstructive material – were prohibited from the city sewers. And of course, metals and cyanide and oils figured in that.

At this point I would like to say that we should not be so parochial as to sit here with blinders on and address ourselves only to trace metals. When you talk about environmental impact you should also consider the refractory organic compounds, which may have very insidious effects or may have synergistic effects because of organometallic compounds. However, we did organize and implement this program, and we were the first coastal city to do so.

As a reward for all our diligence, we found ourselves summoned by the United States Environmental Protection Agency and by some zealous Federal attorneys only a few months ago to appear before the bar of justice and account for our dilatory inaction. The thesis of the Federal attorney was that I must be some kind of shambling Neanderthal who needed to be dragged into the 20th century. Didn't I know about the effects of mercury and cadmium? Didn't I know?

Yes, I do know. I have been in close association with Dr. Michitaka Kaino of Tokyo who fought the famous Minimata case. Just a year ago I stood on the streets of Osaka, Japan, carrying a picket sign along with the students to protest the cadmium discharges that led to the Itai Itai disease. The Federal attorneys wanted me to be aware of the impact of metals, and they wanted our requirements regarding them to be even more rigorous than the Federal Government's. I am a very pragmatic person. Life is not that simple. I have appealed publicly and I am doing so now; but now I know the Federal Government is going to act. For years we have been saying, let the Federal Government set standards for toxic materials throughout the country on an equitable basis and rational basis. We will rigorously enforce them for the wet industries in New York City. I don't want them to be able to move 2 miles away across the Hudson River and take refuge there. There should be no place to hide. These standards should be leveled across the board. The new law for which Congress overrode the President's veto calls for just such promulgations of standards, and we're eagerly awaiting them.

Meanwhile, we have moved vigorously. At a time of austerity in the city, Mayor Lindsay gave me an additional staff, an additional special task force of one of my industrial waste sections of 15 people with the vehicles and the laboratory support and the ancillary clerical support – just to concentrate on intensive policing of metals discharges. Now being an engineer, I am enamored of numbers. Much of the talk about this problem has involved emotion and hysteria rather than real figures.

For example, the specter has been raised that by marine sludge disposal we are creating a dead sea offshore, and that this dead sea was discharging a terrific concentration of metals. If you look at the real figures you will find that dredge spoils and construction debris were actually contributing more metals than the sludge. You would also find that the ambient waters in and around New York City had metals concentrations that were lower than those for the United States Public Health Service drinking water standards. It is very significant that the sludge itself is highly visible. Well-digested sludge is a black, tarry fluid – a viscous fluid. It's much more highly visible than the well-dispersed effluents in the inshore receiving waters. But one discharge from New Jersey, in our Upper Bay, right within spitting distance of downtown Manhattan, has six and one-half times as much BOD as all the BOD of our sludge discharged offshore and with tenfold more metals right inshore. I think it was a reasonable, rational judgment to move the discharge offshore and protect the precious inshore estuarine environment. That's the classical spawning ground of the marine biota. That's the area through which the anadromous fish move as they go up the Hudson. I think that judgment is paying off for us in the restoration of our inshore estuarine precious dissolved oxygen. In studying the metals, however, I wanted to know the actual mass balance of the metals, the quantitative movement.

There was some simplistic reasoning: just nail the electroplaters and you have solved the problem. New York City is not a big wet industry town, but we have about 200 electroplaters. We have sampled every one of them. When I say samples I don't mean grab samples; I mean around-the-clock samples, seasonal sampling to go through all the cyclic and seasonal changes. We have a pretty good fix on their discharges. But I wanted to go one step further. I do a lot of other industrial waste analyses, and I have now started a new procedure. If my men are analyzing fat rendering plants, fish smoking plants, or textile processing plants, they also do analyses for metals to get an idea of the total metal output of all industries and not just those classically associated with metals. I have also prepared charts showing the hierarchy of metals of various big cities in the United States. There is one that really interests me, and that is Grand Rapids, Michigan. It stands head and shoulders above everybody else.

I am trying to get figures on the metals problem so we can make rational decisions where to concentrate our efforts. We have nailed the electroplaters right now. Currently I have in my hand about 80 stipulations from the electroplaters that are being implemented; the rest are being summoned, many each week. We are going to bring them into line, and it has already had a profound effect.

However, when you look at all the sources of metals in megalopolis (and I have a very good way of finding them

I just checked the effluent to my treatment plants) you find some very interesting things. I'd like to nail the culprit, for example, who puts in one-fifth of all the copper coming out of New York City. By now you don't want to hear that trite cliche from Pogo, "We met the enemy and he's us." You've heard that. But I met the enemy; it was me. I account for 22 percent of the copper in the water supply (and hence the sewage) by the copper sulfate that I add in the upstate reservoirs for algae control, and I will continue to do so. I find there is also a measurable amount of zinc in the water supply. You say it isn't much, but we do consume 1.35 billion gallons of water each day in New York City. So if you want to express it in terms of pounds, it would be substantial – as much as 350 pounds of copper.

I proceeded to look even further for sources of metal around our city. I am familiar with the lead emissions – you know, with all that lead that's emitted and solubilized and that Dr. Jacobs hasn't taken care of yet. Where does it go? It is eventually flushed along into a catch basin, into the sewer, and into our treatment plant. Eventually some of it that's not precipitated is going to go out into the receiving waters. They don't have to worry about the stack emissions. Dr. Francis says don't worry, it's 10 ppb not ppm (you know mercury). But all of this is going to get caught by the rainfall and all of it's going to wind up in the receiving waters.

Then I thought of something else. If you look around the city, whether it's New York City or Columbus, Ohio, you will see some corroding car bodies. You look at some galvanized fences and you say that the galvanizing looks a little gray now. What happened to the zinc? Where did it go? It's been solubilized. Where's it going to wind up? It didn't evaporate. It's going to wind up right down in the sewer and eventually in the sewage treatment plant and in our receiving waters. I tried to explain this once to a Corporation Counsel of the City of New York – you know, a very conservative individual, a former Solicitor General of the United States. I was trying to tell him about the amphoteric nature of zinc and particularly aluminum. I tried to explain what an amphoteric metal was, but I wasn't getting through. I tried to point out how these things always wind up in the sewers. "You know, Mr. Counselor," I said, "it's kind of a gay metal that can swing either way." And someone brought the story back to Mayor Lindsay that I was affronting the dignity of his Corporation Counsel. But since he had to take care of the Times Square phenomena, I figured he knew what I was talking about. So you see the galvanizing metals and the corroding facades.

Then I looked at an Assistant Federal Attorney from the Southern District of New York and said to him, "You sir are a polluter and you are a contributor of metals." He replied, "I don't run an electroplating plant." "Mr. Attorney," I said, "do you own your own home?" He replied, "Yes." I asked, "After a while, do you find that you ever have to replace the faucets? Do you find that the sink strainer gets a little corroded after a few years?" He said, "Yeah, yeah." I then asked, "What do you think happened to that corrosion? Do you ever polish anything in your workshop basement?" He answered, "Oh sure, I'm very handy." I said, "What do you think happened to that metal you abraded? Do you ever use any compounds that contain metallic salts you know? Do you know what's in a pharmaceutical compound or medicines you use?" You know, just broken thermometers alone going down the sewers from some bathroom can account for substantial amounts of mercury.

I began to get an idea that sheer residential areas – just people – most of themselves generate metals. So I sent my industrial waste team out to different areas of the city. I knew the industrial areas; I was sampling their wastes. So I sampled areas of one- and two-family homes and modest apartment houses. I went to a big, purely housing complex like Co-op City in the Bronx, and I sampled that. And do you know what I am beginning to find out? I'm going to publish this within a year or so because I keep accumulating data, but I am pleased to tell you now that just like Pogo says, "You and I are in this too, you know."

Without letting up in our relentless quest to get the wet industries to conform, let us just address ourselves to what sheer metropolitan living does. Purely residential areas, and these are just round figures, account for about 33 percent of the copper, 38 percent of the nickel, 23 percent of the zinc, and 57 percent of the cadmium in New York City. Now that may differ in other industrial areas, because New York City is neither a big heavy industry town, nor a big wet industry town. In the classic small town situation, one big plant dominates the town – one big wet industry whose population is larger than that of the entire town.

These figures will change. But since this country is increasingly urbanized, and since these urbs become "slurbs" and suburbs and then coalesce into megalopolises, we should address ourselves to the sheer output of domestic residential living. I invite you to do so at your next symposium, when we talk about what comes out of the automobile and the strip mines (there are no strip mines in New York, to my intense regret; it would solve one tremendous problem of solid waste if there were). When you talk about the sources of metals in our environment, I invite you to consider the source of pure people, and their daily activities. We're great consumers. We are consumers of goods, we are abraders and corroders and users of goods that eventually become soluble metals.

I have been analyzing the metals in the sludge, and I've been talking with the President's Advisory Committee and with CEQ about it. But the truth is that sludge disposal is just another aspect of solid waste disposal.

Anyone here who has a viable solution to the solid waste disposal of any major metropolis has also created a viable solution for the sludge, because the sludge can be merely a top dressing that can ride piggyback on the solid waste. New York City generates up to 30,000 tons a day of refuse, and you know, we're pretty good; we know how to pick it up. But when you pick it up, you've got to set it down somewhere. Everybody wants you to pick it up; nobody wants you to set it down. You all read the environmental journals. Aren't you enamored of returning the organics to the soil?

We're trying desperately to do something. I have used every cubic foot of digested sludge that I could put on completed sanitary landfills to create park area. We've got a beautiful golf course in New York City created on completed, compacted fill and digested sludge (which acts as a synthetic humus, like a topsoil binder). It's not a complete topsoil, and it's not a complete fertilizer; but it can create synthetic topsoil. Nevertheless, we still have the problem of where to set it down. We don't have strip mines, we don't have barren lands, and we don't have any big arroyos or gulches or deserts. We are appealing to the Federal Government: the solution for solid waste disposal transcends narrow political and geographical boundaries. The Federal presence must be felt. We can't go to Chicago as a solution, where there is a man who very complacently says he has solved that problem. He bought 14,000 acres 200 miles from Chicago. It's costing him about $100 per ton (it cost me $12 per ton). He is willing to pay the price; the only thing is, he needs another 50 or 60 thousand acres. If we were to use the Chicago technique, I'd take a good part of southeastern New York State and make it our dump area. And we are talking about sludge only, here.

So obviously the Federal presence must be felt. When the environmentalists ask if you don't want to return the organics to land, my answer is yes, but give me the land. And when we do return the organics to the land, do you know what the Federal EPA says? They say, "Hey wait a minute, fellow. What about that metal burden in there? It's going to leach out, and then what are you going to do?" Irreversible economic ecological damage. We are back to that again; we just toss it from one hand to the other. The options are very limited, and probably the most effective thing to do is to get the metals at the source before they get in. After all, sewage is just slightly used water; that's all it is. The average strength in New York City's sewage is 150 ppm of suspended solids and BOD. That means you've got to work on a million pounds to handle 150 pounds of solids. And if you get the metals concentration down in a fractional ppm range, you'll have to work on hundreds of millions of pounds to work on a fraction of a pound of cadmium or zinc or hexavalent chromium. Therefore, it's easier to get it at the source.

I am just going to leave this one thought with you. It's almost presumptuous of me to talk about metals to this vast array of talent here and to tell you these obvious truisms. But each of you interact with a Federal agency; some of you are a part of a Federal or State agency. My appeal to you is this: that decisions should be made on rational numbers, not on that nice round figure of zero. Because, you know, that's just a nice goal. Consideration should be given to the normal ambient level of metals in receiving waters. Somebody just mentioned a word about vanadium; but I remember reading about 10 years ago in the Scientific American that vanadium plays an important part in the life cycle of sea salps. We know that there are normal metal concentrations in the ambient waters. Our effluent standard should be geared to some rationale, with full knowledge that there may be synergistic effects, with full knowledge that discharge into estuarine waters may permit shellfish to concentrate metals.

I have touched a number of bases, but I want to emphasize two things. First, there are many inputs to our environment besides strip mines, electroplaters, and wet industries. One such input is sheer metropolitan living itself. Second, I think we should be in an intense data gathering situation now to determine the base line data of our environment of metals. In that way, we can make judgments on the basis of real figures rather than on hysterical emotion.

SESSION IV
MONITORING FOR TRACE METALS IN THE ENVIRONMENT

Chairman:

R. Rabin
National Science Foundation

MONITORING SESSION – CHAIRMAN'S OPENING REMARKS

R. RABIN
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Concern for the health of man and his global life-support system has spawned an era of ecological logorrhea, the nucleus of which is the term pollution. However confusing and inconclusive the debate, collective public opinion on pollution is easily formed when the senses are directly affected. And when pollutant concentrations are sufficiently high and resultant damaging effects are readily perceived, the impacted population may obtain redress given the motivation and needed legal instruments. Of course, this represents an extreme; the tip of the pollution iceberg.

In the present social climate, which encourages a more thorough and scholarly assessment of man's activities and their environmental consequences, we face new realities. These relate to the quintessential and vexing question of how one scientifically and legally defines a pollutant or contaminant. Although other considerations subserve this question, they too must be examined. For examples:

A. Very often the substance is only detectable in trace concentrations, i.e. at levels of micrograms or less per gram or per liter. Analytical methods to separate the contaminant from complex mixtures, identify and measure it are time consuming and expensive. Even state-of-the-art methods may be relatively insensitive or inaccurate, and rely on trouble-prone instrumentation. There may be inadequate standard reference materials against which the suitability of a method can be calibrated. Improper sampling and sample handling and storage may introduce substantial errors into the data output.

B. In natural habitats the toxicity of a contaminant may be expressed so subtly that months, possibly years, may elapse before ecological perturbations are evident. Thus, the consequences of threshold effects are no less important to the population ecologist than they are to the biochemist or toxicologist. They eventually relate to the elasticity of biotic communities, i.e. their ability to withstand irreparable harm from assault on their most sensitive members. Spatial considerations in the contaminant-target relationship also complicate matters since accumulation and toxicity may be perceived far downstream or downwind from the point of release.

C. The cause and effect association between compound and target apparent in the field may originate with a parent compound whose structure and properties have changed during transport. The evolution of peroxyacetyl nitrate (PAN) in smog by photolysis, and the methylation of inorganic mercurials are well-known examples. In both cases the end products are more toxic than their progenitors. We recognize with increasing clarity and frequency that knowing only the value for total mercury or cadmium (or whatever element) is not enough; quantifying the biologically active form may be essential.

D. Transport processes themselves are imposingly complex. Much of the tetraethyl lead in gasoline, for example, is emitted in auto exhaust as lead chlorobromide in a population of particulates varying from a micron or less to those much larger in size. Larger particles settle quickly along the roadside in suburban and rural areas. Soil cores, vegetation, and rodents show concentrations of lead diminishing from up to 1000 parts per million (ppm) at the source to a background level of about 20 ppm at a distance of 50 to 100 meters. Collectively, data indicate that man's best natural protection against rurally vented lead is soil, which in its capacity as a vast ion exchange resin, tenaciously chelates the metal under common conditions. But the fine (submicron) particulates are subject to myriad meteorological and climatic variables which have prevented easy development of satisfactory air transport models from line source pollution. In urban areas, where such information is so badly needed, and the soil-to-concrete ratio is much smaller, the movement patterns of lead are largely unknown. Street dust is suspected to be an important reservoir for atmospheric reinjection and for storm drain-carried lead. From the latter, lead may be partitioned between sludge after sewage treatment, and rivers and streams in both soluble and sediment bound states. Zoologists at the University of Illinois have shown that bloodworms inhabiting sediments near the water-sediment interface are avid concentrators of the metal perhaps constituting an important link in lead transport in aquatic food chains. Aquatic biologists at the University of Missouri, Rolla, and the University of Colorado have found that algae in streams receiving effluents from metals mining and milling operations concentrate trace metals in the range of hundreds to thousands of ppm.

E. The signal-to-noise ratio in engineering parlance is also applicable to the study of trace contamination. Unless background levels contributed by volcanism, rock weathering, soil formation and breakdown, and other natural processes are accounted for, the importance of some human contributions may be overemphasized. While the environmental release of cadmium seems almost entirely man's doing, perhaps more than 50 percent of circulating global mercury is a consequence of a complex natural cycle. Geographical medicine is a field of study which relates natural excesses and deficiencies of elements to human and animal diseases. Its potential to contribute insights to the signal-to-noise enigma could be more fully utilized.

F. The scientific aspects alone of metal contaminant research problems require expertise in many disciplines. The research team approach, beside demanding individual scholarship, needs dynamic management. In the university milieu the traditional disciplinary and departmental organization may impair the formation and function of interdisciplinary amalgams. That they do exist and are performing productively, however, severely tests the pessimists' hasty generalizations of several years ago. Perhaps even more important is the fact that universities haven't found it necessary to scrap and rebuild their structures to accomplish this.

The principal concerns of the scientific community are, as I see them:

1. Determining the levels of potentially or overtly toxic substances in the environment;
2. Assessing the effects of these levels on man, animal, and plant communities;
3. Relating these findings to methods of control.

To address these concerns I recognize research opportunities in that:

1. Toxic or hazardous substances must be separated from complex mixtures, identified and measured, or analyzed in situ;
2. The movement of contaminants and their rates of flow through environmental media must be traced from their sources to ultimate deposition sites;
3. Target organisms along, and at the end of, the routes of flow and their sensitivity to noxious agents must be determined;
4. The complex relationships between biotic communities and the effects of the biologically available toxicants must be understood;
5. Research results should suggest improved monitoring systems and, when warranted, ultimately aid in devising technological, legal, and economic abatement or control measures.

When considering which contaminants merit our attention, I suggest that we contemplate the following aspects:

1. Intrinsic biological risk;
2. Geographical dispersion;
3. Quantity and persistence in the environment;
4. A presumptive tendency to accumulate in the food sources of man and other biota; and
5. Difficulty of avoidance based on extant use patterns and current technology.

Research and monitoring is anchored in analytical methodology. The perception and measurement of contaminants in biota and environmental media, particularly in trace concentrations, form the common denominator relating levels, effects, and efficacy of instituted controls. Analysis in no less critical to the researcher than to the monitor, standard setter, polluter or inforcer.

MONITORING FOR TRACE METALS IN THE ATMOSPHERIC ENVIRONMENT: PROBLEMS AND NEEDS

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It is difficult to write a paper of readable length on such a broad topic. It takes arrogance or naivety to even attempt it. However, not to do one's best shows a contentment with ignorance. Not being so contented, the author wishes to plead only humility, leaving the reader to choose the motive.

In order to properly scale the task we should consider the magnitude (or better stated, the lack of magnitude) of the subject in mind. If we wish to end up with a reasonable approximation of the concentration of a trace element floating in the free atmosphere, we must first realize that a sampler is a concentrative process. For example, the high volume sampler will draw approximately 1.5 to 2 cubic meters of air through the filter each minute. Usually these will run for 24 hours, representing somewhere between 2200 and 2900 cubic meters of air concentrated on a piece of paper 63 square inches in surface, each inch representing about 40 cubic meters of air. We then take that filter paper, remove the material by extractions, and then institue a subsequent chemical concentrative process. We thus go through two concentrative and one removal process with all the biases, errors, and selectivities involved. Considering all possible points of error, it seems a miracle that we get meaningful results at all. In many unfortuante cases we probably fooled ourselves into thinking so.

We make this example in order to show that indeed there are difficult, but not unique, problems in obtaining elemental analysis in the atmospheric environment. The scope of this paper will be to point out a general procedure, considerations involved, and suggest some needs and solutions to those needs. Since there are as many details in the analytical procedures as there are chemists, we will simply give an outline of a workable procedure with details and examples.

Suggested Procedures in Reaching a Believable Number

The first task that we must do is the obvious literature search. This is an imperative task but should be done with a jaundice eye. There are some base documents which could be suggested at this time. Probably one of the most complete documents of elemental analysis of particulate in the air is a thesis (1) which lists several values of more than 30 elements obtained from both urban sources and the northwest Indiana area (2), as well as data from more remote areas across southern Canada. There are other general documents such as the air quality data from the National Air Sampling Network (NASN) prepared by the Federal Environmental Protection Agency (EPA). The latest completed document is for 1968 values (APTD-0978, 1968). Other more recent information is available through professional society publications. The problem with these documents is that they represent only one site, usually located in the center of an urban area. Exposures of these sites are not all representative of these areas. For example, in Chicago the station is located approximately 15 feet back from one of the most heavily traveled streets and is 12 feet above the ground. Add the fact that it is within 5 feet of a seven-story building, in an area surrounded by even taller buildings, and it is no wonder that this station shows high particulate levels as well as high concentrations of trace metals. This accounts for a tendency toward larger size distributions than other stations which are not located in dust traps.

We can usually find documents on a particular element. Lead, copper, and cadmium have been described in an urban area for six separate days over a network of 50 stations throughout the Chicago and northwest Indiana regions (2). Please see Table 1.

Many older documents cite numbers which can be used as guidelines. For example, prior to 1960 there were over 3,000 references to lead alone. Of course, the more rare the element, the more rare the references in most cases.

Having perused the literature and estimated the size of the needle, we must now choose a method of capture and a method of analysis. In both cases we should concern ourselves with sensitivity. If it is known or suspected that the particle size distribution is such that the particles are less than 1 micron on the average, we should consider more positive, smaller pored filter papers. Good references are obtained from companies making filter papers such as Gelman Instruments, Ann Arbor, Michigan and Millipore Corporation, Rosemont, Illinois. If the average size of the particle is unknown or it is larger in the mean than 1 micron, a standard, inexpensive high volume filter is probably as good as any device in capturing a larger amount of material over a reasonable period of time.

Now comes the problem. If we want a large amount of sample we use the whole filter, which then could draw high contamination or blank value from the paper. On the other hand, we can choose a smaller part of the filter paper, decreasing our blank substantially, but also decreasing our sample. A convenient method of optimizing this problem is to calculate a signal, i.e., concentration, to blank ratio which automatically dictates that before any sampling is analyzed a thorough investigation concerning the contamination of the filter media be made. Tables 2 through 8 are examples of the kind of thoroughness required for selection of the filter for impaction media for subsequent analysis by neutron activation (3).

Assuming that we have acceptable blank levels, we must decide how much material to capture in order to obtain a meaningful sample. The amount will be dictated by the method of analysis. Now we see that we have to make two decisions in fairly rigid tandem. We either choose the time period of investigation and obtain a method capable of the necessary sensitivity, or we choose a method and alter our sampling time or amount necessary for capture accordingly. In most cases, this is a moot point because the equipment is already purchased before the counter decision has been made. Unfortunately, too many times, the net result is that the micro-structure desired is elusive due to the lack of

TABLE 1 CONCENTRATIONS AT MAXIMUM, MINIMUM, AND CONTROL STATION

Element	Concentrations ng/m³			Concentration Ratios	
	Maximum	Minimum	Niles	Max/Min	Max/Niles
S	18,000 (10,000)*	3,000 (3,000)	11,000 (5,000)	6 (9)	1.6 (1.0)
Fe	13,000 (3,000)	1,420 (120)	1,900 (100)	9.7 (3)	7.2 (2.0)
Ca	7,000 (700)	1,410 (200)	1,000 (200)	5.0 (0.7)	7.0 (1.5)
Cu	4,000 (200)	25 (4)	280 (20)	160 (30)	14 (1.5)
Al	3,100 (300)	1,375 (70)	1,200 (70)	2.3 (0.3)	2.6 (0.3)
Mg	2,700 (1,000)	530 (300)	500 (300)	5.1 (3)	5.4 (3)
K	1,860 (110)	730 (90)	720 (50)	2.5 (0.4)	2.4 (0.3)
Zn	1,550 (200)	100 (12)	160 (20)	16 (2)	9.6 (1.4)
Na	500 (50)	160 (20)	170 (20)	3.1 (0.4)	2.9 (0.4)
Mn	390 (50)	63 (3)	62 (3)	6.2 (1)	6.3 (1.0)
Br	300 (30)	26 (2)	38 (6)	12 (1.5)	8.1 (2)
Ti	280 (50)	120 (25)	120 (25)	2.3 (0.7)	2.3 (0.7)
Cr	113 (20)	6.2 (0.8)	9.5 (0.8)	18 (3)	12 (2)
Sb	31 (3)	2.2 (0.2)	6.0 (0.3)	14 (2)	5.3 (0.7)
V	18.1 (1.5)	4.01 (1.0)	5.0 (0.3)	4.5 (1.2)	3.6 (0.4)
Ce	13 (1.5)	1.4 (0.1)	0.82 (0.06)	9.3 (1)	16 (4)
As	12 (2)	2 (1)	4.6 (2)	5 (4)	2.6 (1.2)
La	5.9 (0.4)	0.9 (0.3)	1.3 (0.3)	6.6 (2.5)	4.5 (1.0)
W	5.6 (1)	0.3 (0.3)	0.4 (0.2)	19 (19)	14 (7)
Ag	5 (2)	0.5	1	10	5
Hg	4.9 (0.9)	0.8 (0.3)	1.8 (0.3)	6.1 (3)	2.6 (0.7)
Se	4.4 (1.2)	0.8 (0.5)	2.5 (0.5)	5.5 (3)	1.5 (0.6)
Ga	3.5 (1.0)	0.25 (0.15)	0.9 (0.4)	14 (10)	3.9 (1.2)
Sc	3.1 (0.3)	0.92 (0.1)	1.2 (0.1)	3.4 (0.4)	2.6 (0.3)
Co	2.6 (0.6)	0.47 (0.06)	0.95 (0.1)	5.5 (1)	2.7 (0.7)
Th	1.3 (0.4)	0.17 (0.02)	0.27 (0.08)	7.6 (2)	(1.0)
Sm	0.65 (0.20)	0.17 (0.02)	0.24 (0.03)	3.8 (1.5)	2.0 (0.4)
Eu	0.17 (0.03)	0.06 (0.01)	0.055 (0.02)	2.8 (0.5)	3.0 (0.5)
In	0.15 (0.06)	0.03 (0.03)	0.04 (0.03)	5 (5)	3.7 (3)

(After K. Rahn 1971)
*Large filter impurity correction.

sensitivity and specificity of the analytical technique and instrumentation.

Following the same argument, we usually try to increase the effective sensitivity of our instrumentation by separating the particulate material from our capturing media or by extracting the interesting part. We then must concern ourselves with the efficiencies of extraction and the possible interference due to elements of similar chemical nature. At this point the arguments take place among the chemists, and I desist from pursuing this particular subject any further except to say that the task must be to increase the sensitivity of the instrumentation and to eliminate those separations and subsequent concentration techniques which require very pure reagents and the precision of a dedicated watchmaker.

Assuming the above considerations are well under control, we must now estimate the number and locations of the samples needed for proper description of the phenomena of interest. Once the number of samples has been estimated, treble it, for experience so dictates. This will cause us to calculate the time it will take to analyze all our samples (which usually forces the researcher back to the drawing board to narrow the scope of study and/or to select a new method of analysis). In some cases, time advantage can be found through parallel analysis rather than serial, one at a time, methods. For example, if equipment is available we can batch the preparations and chemical procedures. Anodic stripping voltametry (ASV) has an advantage, inasmuch as it is a timed analysis which allows multiple platings sequenced a minute or two apart. The samples are analyzed and changed before the next sampling sequence is ready for stripping (2).

Throughout this whole procedure we must carry along blanks of the capturing media precisely the way we would handle the media and sample itself. For example, filter papers from the same box should be carried to the site, put on the sampler, and removed without a sample being taken. These samples should be analyzed as if they were real. We can detect and correct for system blanks in this manner if they so occur. This is a primary control method for the media. Of course, good chemical standards should also be prepared and carefully checked.

We will pause here, after describing many of the above problems, to clearly state the needs to this point. They are as follows:

1. A more positive capturing technique.
2. The capturing media must be relatively clean, homogeneous, and have a listed assay as required by any chemical reagent.
3. We must eliminate many of the extraction, separation, and chemical concentrative steps by increasing the sensitivity of the physical measuring devices.

Having forged onward to the obtaining of several numbers, and having full confidence in those numbers and their error limits, we will now hypothesize that we have efficiently captured the material in question, have analyzed that material for the element(s) so desired, subtracted the blanks, eliminated its systematic errors, and have a reasonable understanding of the concentrations. We now proceed to the next step.

Data Representation and Interpretation

Two primary areas to consider in interpretation of your hard-won data are the manner of presentation and pertinent auxiliary information. These considerations probably take as large a share of failures as do the problems with analytical techniques.

This first point is axiomatic. We should not involve ourselves in securing or interpreting atmospheric samples of air quality without the advice and consultation of a reasonably qualified applied meteorologist. With even brief consultation periods, we can eliminate many potentially fatal mistakes. A case in point is that of a renowned researcher who carefully correlated excess deaths of infants and aged persons downwind of a nuclear power plant. His evidence and conclusions showed that there were approximately 10 percent excess deaths in an area away from the prevailing wind. After presenting his evidence at more than one meeting, as well as causing civilian alarm by newspaper releases, a meteorologist pointed out that the barbs on the wind direction lines are customarily put on the end of the line pointing in the direction from which the wind is blowing. Thus this nonmeteorologist statistician had proven that nuclear radiation from this particular facility was good for children and the aged. This example illustrates one of the obvious needs for a meteorologist to assist in the design and interpretation of the data.

Associated data could take the form of the total suspended particulate weights to indicate the percentage of total sample with respect to the elements in question. Wind parameters, direction, and speed are needed to estimate the transport characteristics so we can subsequently identify the source region. Finally, an estimation of the source inventory is desired in order to validate our source strength predictions or to suggest new hitherto unknown sources. These inventories should take the form of both point source and area-wide source estimations. Examples of this technique are presented in Figures 1 to 8, representing an area-wide distribution of suspended particulate, its lead fraction, selected wind roses, and an estimation of the urban traffic densities. The weakest point in this presentation, as often is the case, is the emission inventory. Copper and cadmium are presented for the same day but without emission inventory data. Another set of data are shown in Figures 9 to 12 (2). Depicted here is the dependence of lead levels on wind direction adjacent to a large metropolitan area. It should be noted that the maximum occur shortly after the wind direction comes from the sector containing the large city. The minimum occur outside that sector. It will also be noted that the lead levels reached a detectable minimum while the copper and cadmium levels continued to drop below detectable limits, representing a background value for lead. We present this data in order to show that proper interpretation and presentation of associate information leads to much greater wealth of knowledge than simple presentation of the data by itself.

In summary, we should have sufficient information to properly understand the emission strengths and transport characteristics of our contaminants, as well as the amount of receptor exposure (concentration).

We have shown two methods of data representation which inherently contain compilation and correlation difficulties. The first is that of isopleth analysis where, for example, concentration values may be too large to conveniently plot and/or where isopleth gradients are too steep to draw a distinguishable line. When comparing air quality data directly to meteorological data, a second difficulty, that of correlation, is made evident. To a statistician it is obvious that if time was held constant, correlations between trace metal concentrations and wind speed, wind direction, humidity, and etc. would probably lead to poor or superfluous conclusions. Plotting the information adjacent to each other, we realize a time delay in the advection of the material from the source region to the sensor. The conclusions are thus convincing without being lost in the statistical formulations. Please see Figure 10.

We cannot represent such area-wide data in straight concentration isopleths, but in percentages of the maximum. Figures 13 and 14 represent the usefulness of such techniques. In this presentation we plot logarithmic percentages of concentrations from 50, 25, 12, 6 percent, and so on. The advantage is that we have a graphical means of interpreting source regions (or lack thereof) in a relatively uncluttered manner while still maintaining sufficient detail. Point sources become obvious due to the reasonable clustering of the isopleths. If there are no local sources we can draw few lines of constant percent due to the lack of variation in concentrations. These two graphs indicate separate wind directions which easily indicate a source region west and between Stations "J" and "G".

If a large number of days or periods of samples can be obtained, pollution roses such as shown in Figure 15 are very helpful. Nonvariation in the concentration of a pollution rose indicates that either the material is fairly universal throughout a large region and is background in origin, or that the material is emitted uniformly throughout the region (e.g. lead).

A final point should be made. In circumlocution, it is important to carefully select and properly describe the location of the sampling points. Again, a reasonably competent applied meteorologist can be of invaluable assistance. At the onset of this article the location of a certain continuous air monitoring project station (CAMP) was discussed. The advisability of such a location is not to be criticized if we fully understand and desire to measure that particular situation. We can severely criticize anyone who extends his interpretation of data gained from such a biased location to the total region. In other words, we should use multiple sampling points to describe a region's exposure to any contaminant. Single point source sampling should be used only when the location is properly described in sufficient detail for the reader who may use such data to know precisely the limitations of such data. Thus, we need a careful selection of sampler sites.

CONCLUSIONS

Our conclusions will be quite brief and simple. After discussing the above considerations pertaining to site locations, analytical techniques, interpretations, and methods of presentation, it becomes quite apparent that if we are to succeed in the business of advancing the knowledge of elemental concentration distribution in the atmospheric environment we must rely upon the experience and expertise of several disciplines. We must conclude that any meaningful experiment will be well thought out and discussed in detail with persons of many disciplines in conjunction with the researchers. Our purpose is to convince one that this approach is mandatory.

If one is to not sentence his hard earned numbers to the archives of perfunctory literature, we would suggest that a multi-discipline team approach be chosen. It is quite evident that our utmost and immediate problem is to meet the obvious needs.

TABLE 2 FILTER MATERIAL INVESTIGATED

Filter Material	Manufacturer's Name	(Key)	Manufacturer	Specifications	Comments
Polystyrene	Microsorban	(PS)	Delbag Luftfilter (Germany)	–	No longer available
Polystyrene	Microsorban	(DMS)	Delbag Luftfilter (Germany)	–	Presently available
Cellulose–organic binder	Whatman No. 41	(W41)	W. and R. Balston Ltd. (England)	–	Tightly woven
Cellulose	–	(C)	C. H. Dexter and Sons (USA)	–	Loosely woven
Membrane cellulose esters	MF-Millipore	(HAWPO25)	Millipore Filter Corp. (USA)	Pore size 0.45 um, diameter 25 mm	–
Membrane cellulose esters	MF-Millipore	(HAWPO47)	Millipore Filter Corp. (USA)	Pore size 0.45 um, diameter 47 mm	–
Membrane cellulose esters	MF-Millipore	(AAWPO25)	Millipore Filter Corp. (USA)	Pore size 0.8 um, diameter 25 mm	–
Membrane cellulose esters	MF-Millipore	(AAWPO47)	Millipore Filter Corp. (USA)	Pore size 0.8 um, diameter 47mm	–
Membrane cellulose acetate	Cellotate	(EHWPO47)	Millipore Filter Corp. (USA)	Pore size 0.5 um, diameter 47mm	–
Membrane cellulose triacetate	Metricel	(GA-6)	Gelman Instrument Co. (USA)	Pore size 0.45 um, diameter 47mm	–

(After K. Rahn 1971)

TABLE 3 FILTER IMPURITY LEVELS (ng/cm²)

	PS	DMS	W41	C	HAWPO25	HAWPO47	AAWPO25	AAWPO47	EHWPO47	GA-6
Cl	3,000	27,000	100	300	1,000	1,000	1,700	1,000	1,800	600
Br	25	1,000	5	20	4	3	< 5	< 2	6	4
S	–	±30,000	–	6,000	–	–	4,800	–	–	–
Na	80	90	150	700	600	330	520	400	1,800	2,200
K	20	8	15	200	130	100	120	100	–	–
Mg	< 200	<1,500	< 80	2,400	< 300	< 200	400	200	–	–
Ca	300	300	140	3,800	670	250	500	370	570	1,250
Ba	7,000	<500	< 100	< 100	< 100	< 100	<100	< 100	–	–
Al	20	20	12	200	20	10	15	10	60	740
Sc	0.04	< 0.01	<0.05	0.2	< 0.05	< 0.01	< 0.01	< 0.05	–	–
Ce	< 0.4	< 1	<0.5	< 0.3	< 0.5	< 1	< 0.5	< 0.3	–	–
La	< 0.2	< 0.1	<0.2	< 0.3	< 0.1	< 0.2	< 0.5	< 0.2	–	–
Ti	10	70	10	50	15	5	10	< 10	–	–
Fe	100	85	40	300	40	<300	80	40	–	–
Mn	1	2	0.5	80	7	2	2.5	2	6	2
Co	0.2	0.2	0.1	0.8	0.2	< 1	0.4	0.1	–	–
Ni	25	< 25	<10	60	< 8	<50	14	< 20	–	–
Ag	< 2	< 2	2	3	< 4	–	< 3	< 1	–	–
Cu	10	320	<4	90	20	40	85	60	25	30
Zn	60	515	<25	30	25	20	10	7	–	–
Sb	2.5	1	0.15	0.5	0.5	3	0.4	1	–	–
Cr	5	2	3	12	15	14	20	15	–	–
Hg	3	1	0.5	3	< 0.4	< 1	< 1	0.5	–	–
V	0.06	< 0.6	< 0.03	0.5	< 0.06	0.09	< 0.2	< 0.05	< 0.05	< 0.05

(–) not determined.

(After K. Rahn 1971)

TABLE 4 SELECTED PHYSICAL PROPERTIES OF FILTERS

Filter material	PS	DMS	W41	C	HAWPO25	HAWPO47	AAWPO25	AAWPO47	EHWPO47	GA-6
Flow rate (1-min.$^{-1}$-cm^{-2}) 20 x 25 cm (effective surface 400 cm^2)	4.5	4.5	4.5	6	–	–	–	–	–	–
Flow rate (1-min.$^{-1}$-cm^{-2}) 47 mm diameter (effective surface 9.62 cm^2)	6.5	6.5	6.5	7	–	2.6	–	4.8	2.6	2.6
Flow rate (1-min.$^{-1}$-cm^{-2}) 25 mm diameter (effective surface 3.68 cm^2)	12	13	13	17	4.3	–	7.3	–	–	–
Retention (%) of 0.3 μm D. O. P. aerosol ‡ (25 mm diameter)	99.96	99.95	99.7	–	>99.98	–	99.97	–	–	–
Retention (%) of 0.3 μm D. O. P. aerosol ‡ (20 x 25 cm)	99.8	99.7	91	80†	–	–	–	–	–	–
Volume filtered at 10% reduction in flow ‡ (m^3 air/cm^2 filter)	48	35	2.0 2.8*	>50*	4.1*	4.1*	6.3	6.3	–	–
Thickness (mm) ‡	–	–	0.25	–	–	–	–	–	–	–
Tensile strength (kg-cm^{-1}) †	0.15	0.15	1.41	–	–	–	0.29	0.29	–	–

*Determined by the authors in Ann Arbor, Michigan

†Determined by Brar et al. (1970) for total particulate by weight in Chicago

‡Determined by Lockhart and Patterson (Lockhart, L. B., and R. L. Patterson, In: RL Report 6054, U. S. Naval Research Laboratory, Washington, D. C., 1964.

(After K. Rahn 1971)

TABLE 5 SAMPLE/BLANK RATIOS FOR 25 mm DIAMETER W41 FILTERS, USING NILES, MICHIGAN CONCENTRATIONS

Element	Conc. (ng/m^3)	(Sample/Blank)*		
		1 hr sample	4 hr sample	24 hr sample
Cl	100 †	0.6†	2.3†	12†
Br	70	8	33	160
Na	200	0.8	3	16
K	400	16	62	310
Ca	900	4	15	75
Al	800	40	160	800
Ti	100	6	23	120
Fe	600	9	35	180
Mn	30	35	140	700
Co	0.3	1.8	7.0	35
Sb	2	8	31	160
Cr	10	2	8	40
V	3	> 60	> 230	> 1200
Cu	30	> 4	> 17	> 80
Zn	60	> 1.4	> 5.6	> 28

*For $\genfrac{}{}{0pt}{}{\text{47 mm diameter}}{\text{20 x 25 cm}}$ multiply by $\genfrac{}{}{0pt}{}{0.37}{0.46}$

†From cascade impactor data of same period.

(After K. Rahn 1971)

TABLE 6 SAMPLING TIMES TO EQUAL BLANK VALUES OR DETECTION LIMITS

Element	Sampling time at Niles in hours on 25 mm filter disc to equal:						
	Detection Limit	PS Blank	DMS Blank	W41 Blank	C Blank	HAWPO25 Blank	AAWPO25 Blank
Cl	2	60	500	1.7	4	50	50
Br	0.15	0.8	29	0.15	0.4	0.35	–
Na	0.5	1	0.9	1.5	5	18	9
K	0.1	0.1	0.04	0.085	0.8	2.2	1
Mg	1.5	–	–	–	4	–	1.5
Ca	0.5	0.7	0.6	0.25	5.5	3.8	1.7
Al	0.02	0.05	0.04	0.025	0.3	0.15	0.06
Ti	0.6	0.2	1	0.1	0.5	0.7	0.35
Fe	1	0.3	0.25	0.1	0.6	0.35	0.4
Mn	0.05	0.08	0.15	0.035	4	1.5	0.3
Co	2.8	1.5	1	0.6	3.3	3.5	4
Cu	2	1	25	–	5	5	12
Zn	0.7	2.5	18	–	0.75	2.5	0.6
Sb	2	3.5	1.5	0.2	0.5	2	1
Cr	0.8	1	0.35	0.5	1.5	7.8	6

(–) If for the blank value only a higher limit was found or if it was not determined.

(After K. Rahn 1971)

TABLE 7 POLYSTYRENE-CELLULOSE EFFICIENCY COMPARISON

Element	Atmospheric concentration (ng/m^3)				Concentration ratio
	Polystyrene		Whatman no. 41		What. no. 41/ poly.
Cl	4400	(500)*	7500	(500)	1.70
Br	350	(90)	500	(50)	1.43
S	15	(15)	43	(25)	2.87
Na	900	(150)	1300	(200)	1.44
K	4000	(400)	4200	(200)	1.05
Mg	730	(400)	760	(150)	1.04
Ca	4100	(800)	3900	(500)	0.95
Al	2300	(400)	2800	(200)	1.22
Ga	4.5	(1.0)	4.6	(1.5)	1.02
Sc	4.9	(0.6)	3.4	(0.5)	0.69
Ce	17	(3)	12	(2)	0.71
La	4.6	(0.5)	4.6	(0.5)	1.00
Sm	0.67	(0.10)	0.67	(0.10)	1.00
Eu	0.18	(0.04)	0.13	(0.03)	0.72
Ti	170	(50)	280	(0.03)	1.65
Fe	22,000	(4,000)	15,000	(3,000)	0.68
Mn	240	(40)	280	(30)	1.12
Co	3.9	(0.5)	2.9	(0.4)	0.74
Ni	55	(55)	70	(60)	1.27
W	1.5	(0.7)	<2		–
Ag	3	(3)	2.5	(2.0)	0.83
Cu	130	(20)	160	(20)	1.23
Zn	4400	(200)	4300	(200)	0.98
As	29	(7)	35	(8)	1.21
Sb	21	(5)	21	(5)	1.00
Cr	90	(15)	70	(15)	0.78
Hg	1.7	(1.1)	<1.6		–
V	58	(5)	66	(5)	1.14
Se	16	(3)	14	(3)	0.88
Th	1.0	(0.2)	0.8	(0.2)	0.80

*Large filter impurity correction.

(After K. Rahn 1971)

TABLE 8 IMPURITY LEVELS IN DURETHENE POLETHYLENE, NO. 12010

Element	Concentration ($ng\text{-}cm^{-2}$)
Cl	8 (2)
Br	1.0 (0.5)
Na	2.5 (0.4)
K	1.2 (0.3)
Mg	8 (6)
Al	6.8 (1.0)
Sc	< 0.006
Ce	< 0.009
La	< 0.04
Ti	11 (6)
Fe	<11
Mn	0.10 (0.02)
Co	0.02 (0.01)
Ni	< 1.3
Ag	< 0.3
Cu	1.0 (0.5)
Zn	2 (1)
Sb	0.04 (0.01)
Cr	< 0.3
Hg	< 0.1
V	0.010 (0.003)

(After K. Rahn 1971)

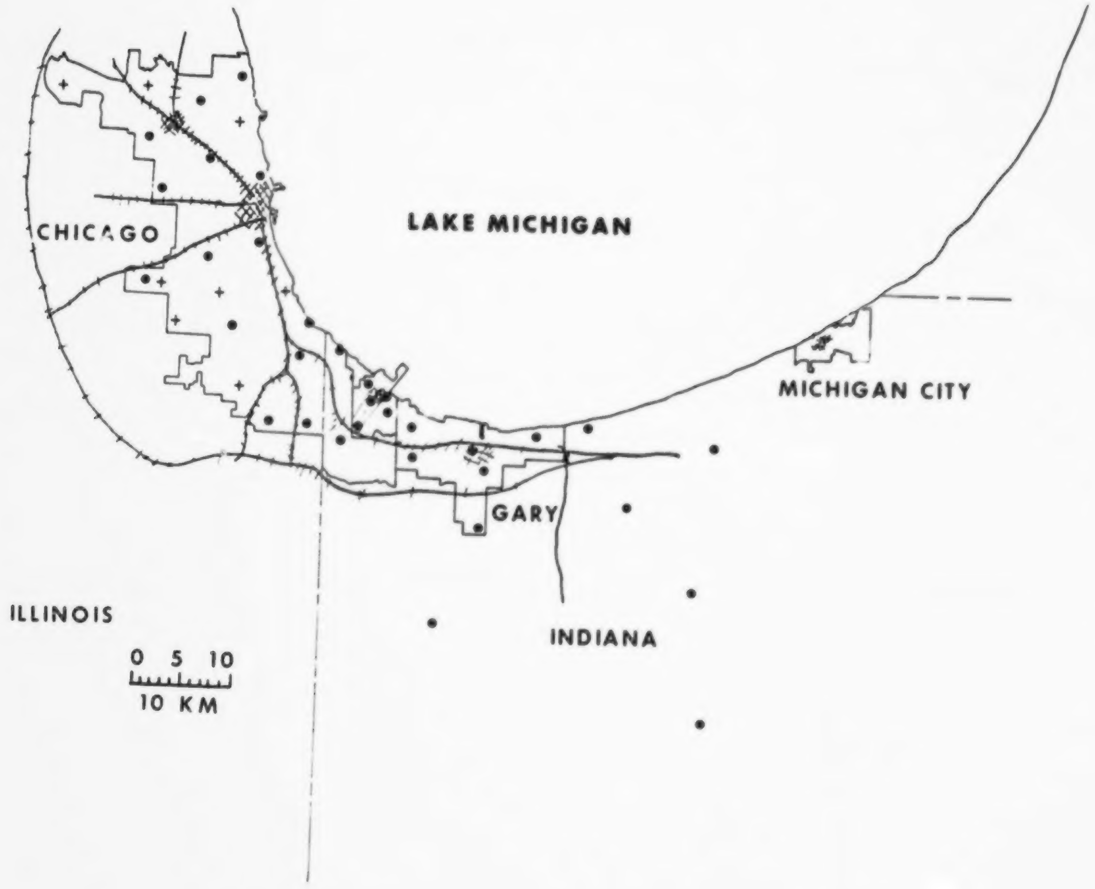

CHICAGO
LAKE MICHIGAN
MICHIGAN CITY
GARY
ILLINOIS
INDIANA
0 5 10
10 KM

Figure 1. Estimation of heavy traffic densities.

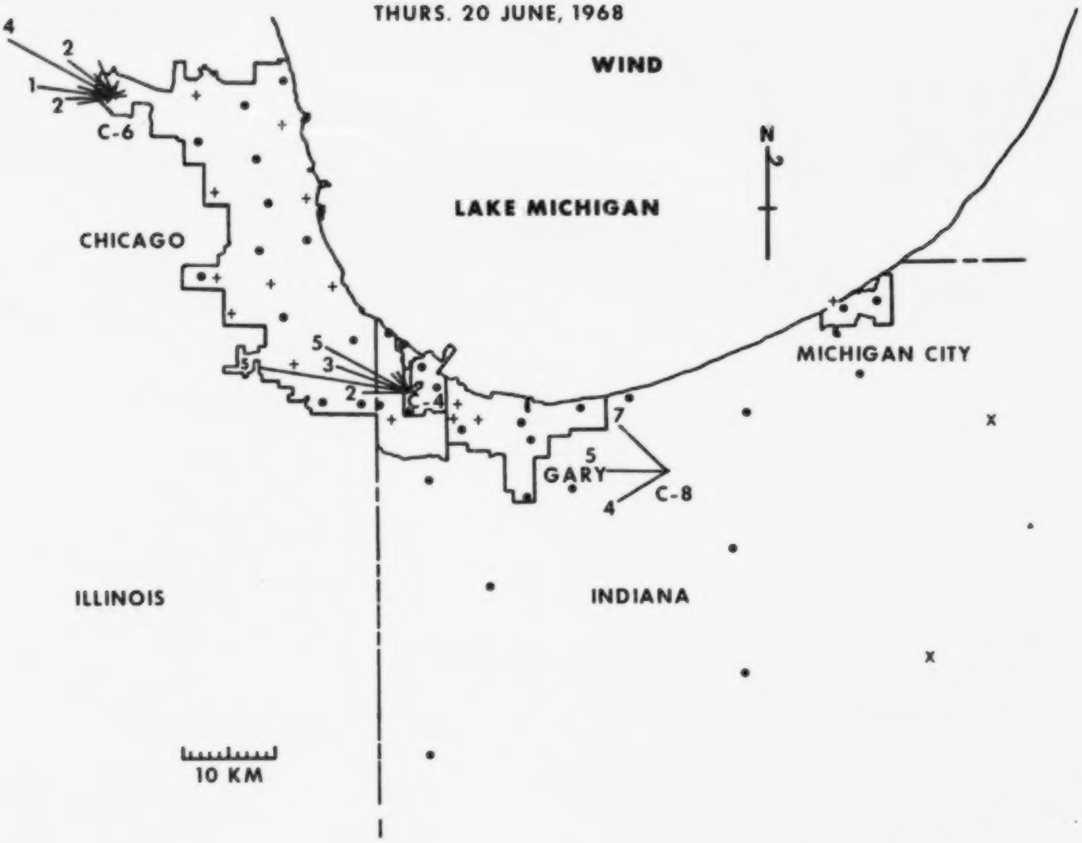

THURS. 20 JUNE, 1968
WIND
N
LAKE MICHIGAN
CHICAGO
C-6
4
2
1
2
5
3
2
C-4
GARY
7
5
4
C-8
MICHIGAN CITY
ILLINOIS
INDIANA
10 KM

Figure 2. Wind direction. Arrows point in the direction that the wind is blowing. The number depicts the number of hours of that direction. C represents number of hours calm (3 miles per hour or less). This convention is opposite to classical methods used by meteorologists.

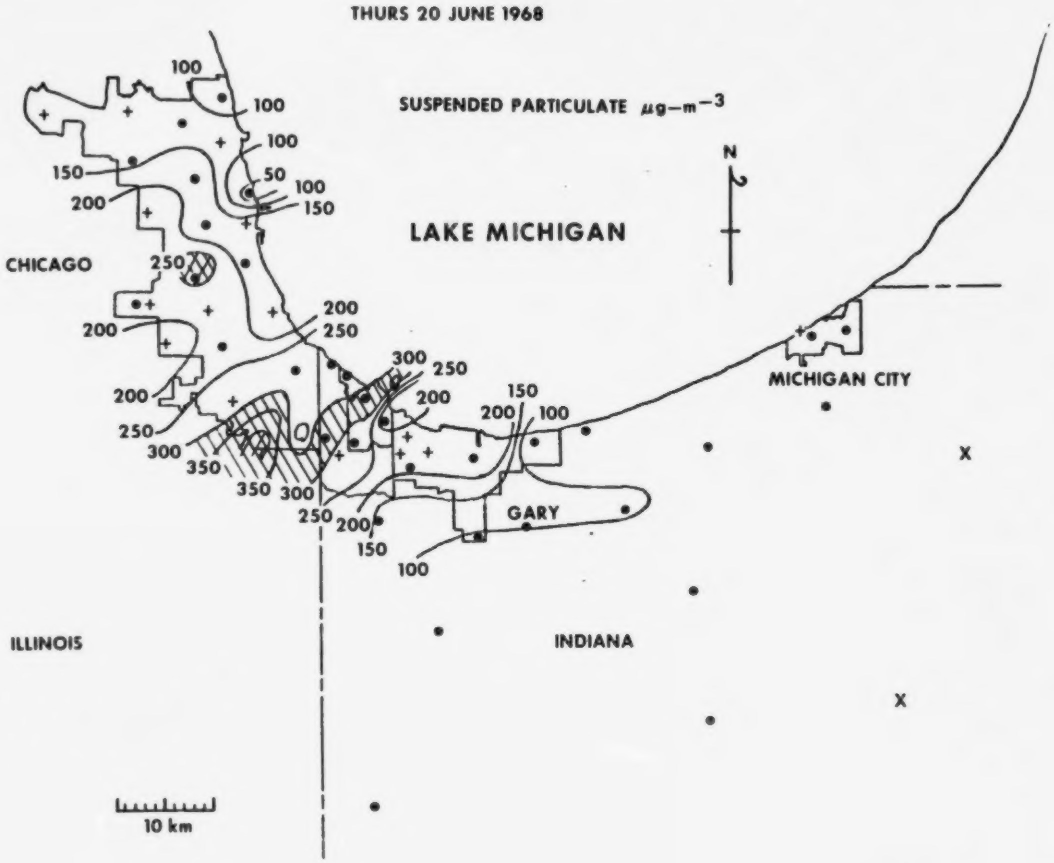

THURS 20 JUNE 1968
SUSPENDED PARTICULATE µg–m⁻³
LAKE MICHIGAN
N
CHICAGO
MICHIGAN CITY
GARY
ILLINOIS
INDIANA
10 km
100
100
100
50
100
150
150
200
250
200
250
200
200
250
300
350
350
300
250
200
150
100
300
250
200
150
200
100
X
X

Figure 3. Isopleths of suspended particulate. Data obtained from 24-hour, high-volume samplers. Original data shown on Figure 4.

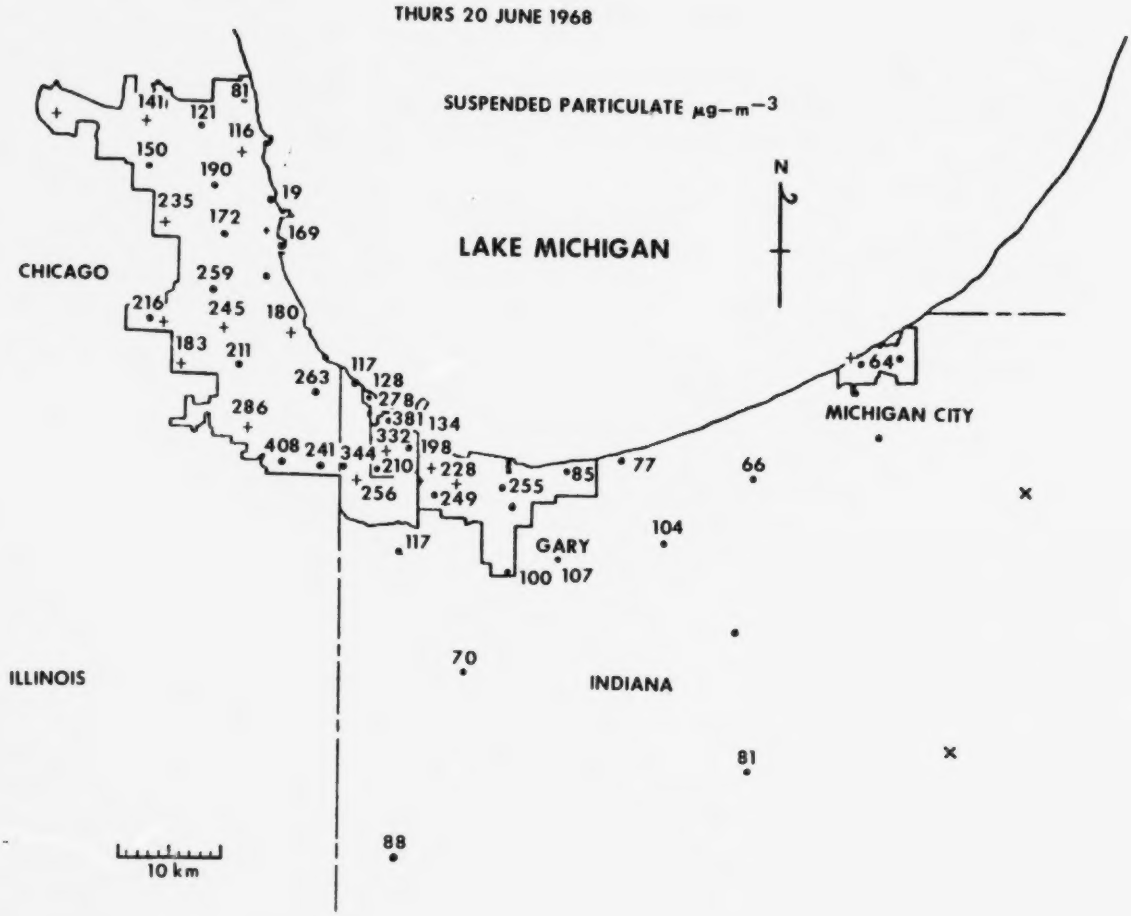

THURS 20 JUNE 1968
SUSPENDED PARTICULATE µg–m⁻³
LAKE MICHIGAN
N
CHICAGO
ILLINOIS
INDIANA
GARY
MICHIGAN CITY
10 km
141
121
81
116
150
190
19
235
172
169
259
216
245
180
183
211
263
117
128
278
286
381
134
332
408
241
344
198
210
228
256
249
255
85
77
66
104
117
100
107
64
70
81
88

Figure 4. Suspended particulate values from individual stations.

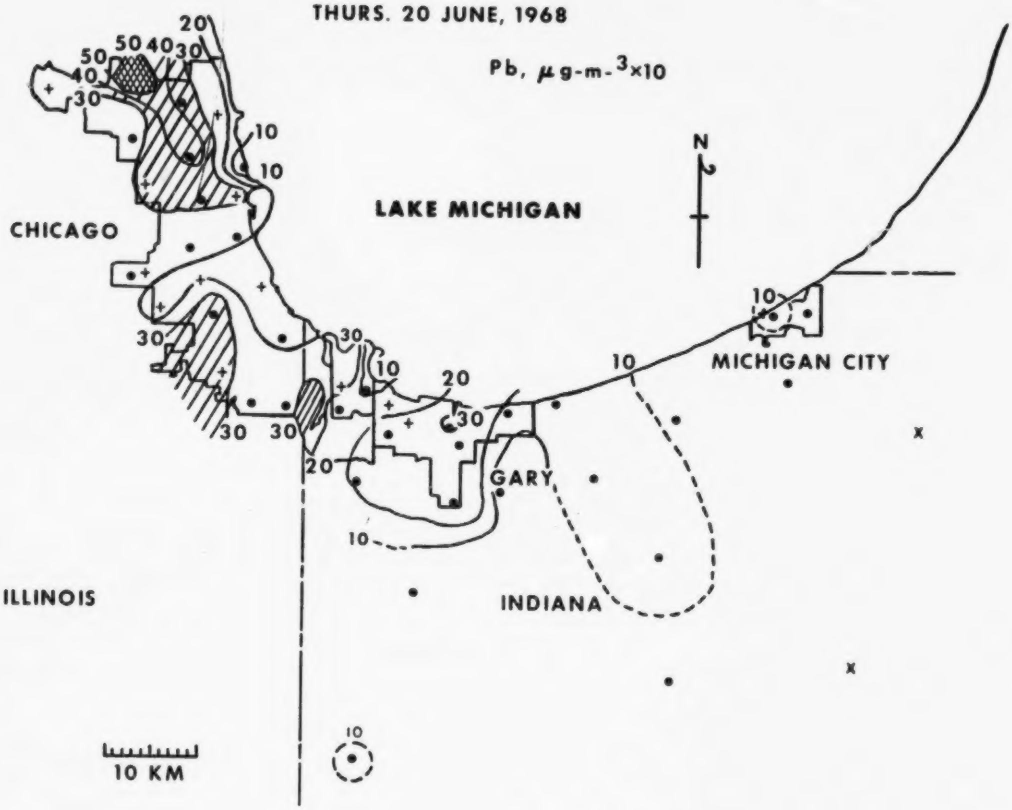

THURS. 20 JUNE, 1968
Pb, μg-m-3×10
N
LAKE MICHIGAN
CHICAGO
MICHIGAN CITY
GARY
ILLINOIS
INDIANA
10 KM
50
50
40
40
30
30
20
10
10
30
30
30
30
10
20
30
20
10
10
10
10

Figure 5. Isopleths of lead fraction from 24-hour high-volume samples.

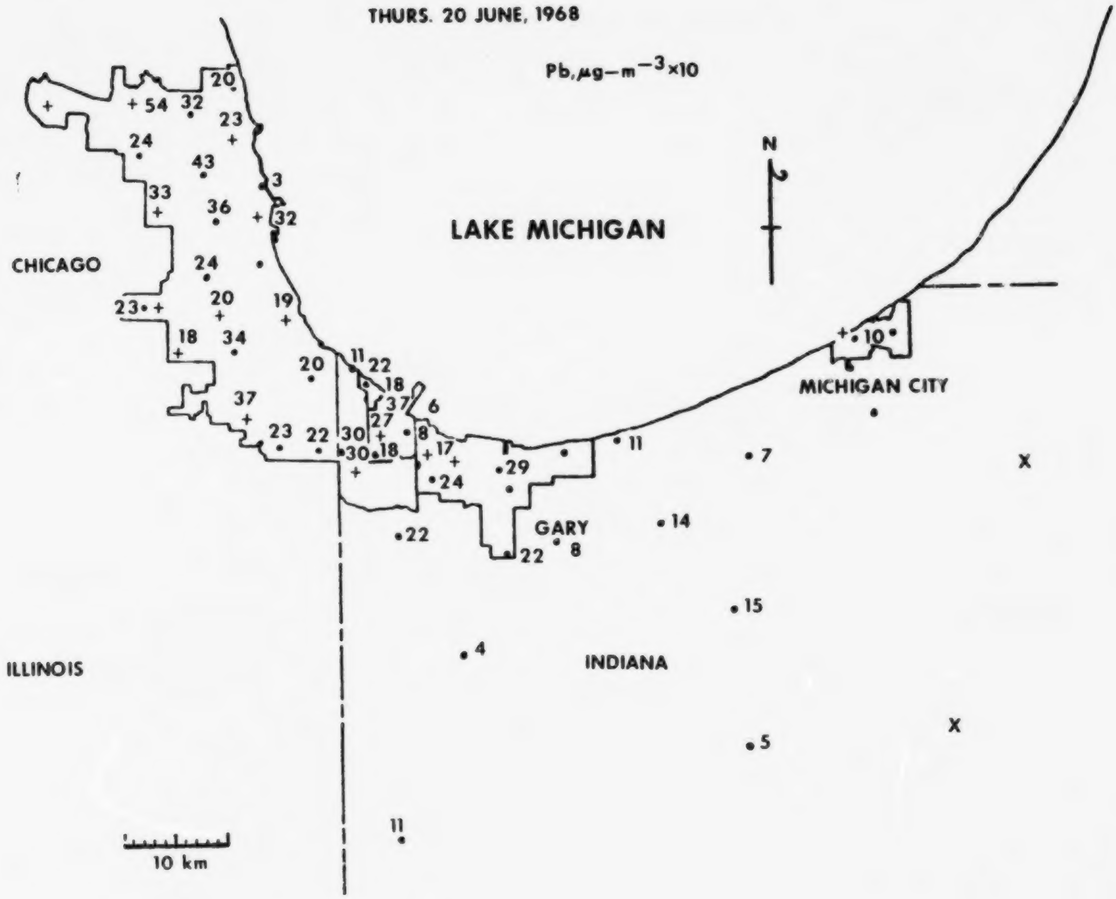

THURS. 20 JUNE, 1968
Pb, μg−m−3×10
N
LAKE MICHIGAN
CHICAGO
MICHIGAN CITY
GARY
ILLINOIS
INDIANA
10 km
20
54
32
23
24
43
3
33
36
32
24
20
19
23
18
34
20
11
22
18
37
6
37
27
23
22
30
30
18
8
17
24
29
11
7
10
14
22
8
22
15
4
5
11

Figure 6. Lead fraction of suspended particulate from individual stations.

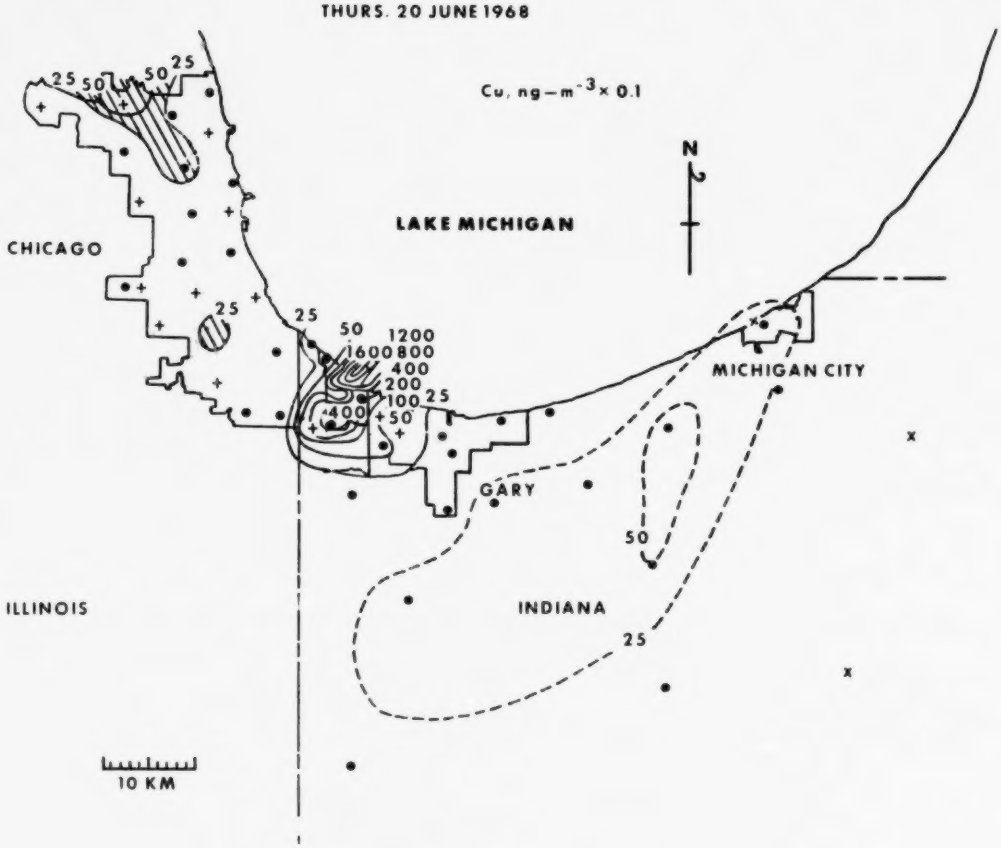

THURS. 20 JUNE 1968
Cu, ng–m⁻³ × 0.1
N
LAKE MICHIGAN
CHICAGO
MICHIGAN CITY
GARY
ILLINOIS
INDIANA
25
50
1200
1600
800
400
200
100
10 KM

Figure 7. Isopleths of copper fraction from 24-hour high-volume samples.

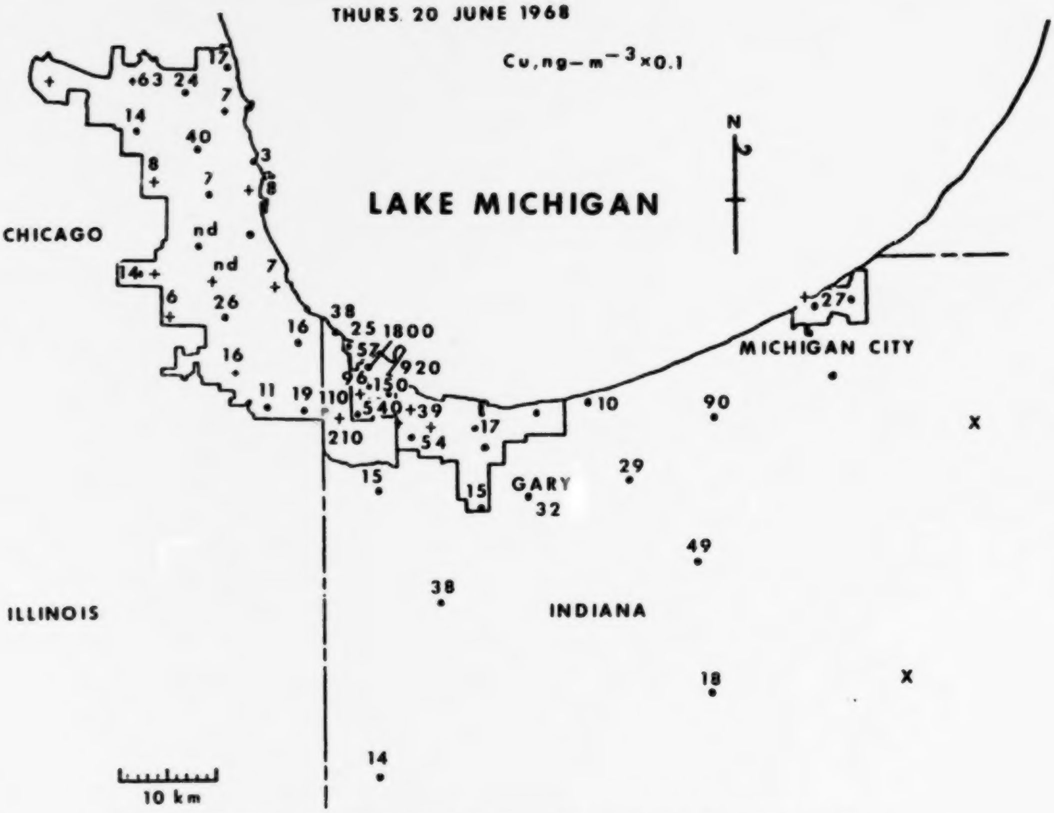

THURS. 20 JUNE 1968
Cu, ng−m⁻³×0.1
N
LAKE MICHIGAN
CHICAGO
MICHIGAN CITY
GARY
ILLINOIS
INDIANA
10 km
63
24
17
7
14
40
8
7
3
8
nd
nd
7
14
6
26
16
16
38
25
1800
57
920
96
150
11
19
110
540
39
210
54
17
10
90
27
15
15
32
29
49
38
18
14

Figure 8. Copper fraction of suspended particulate from individual stations.

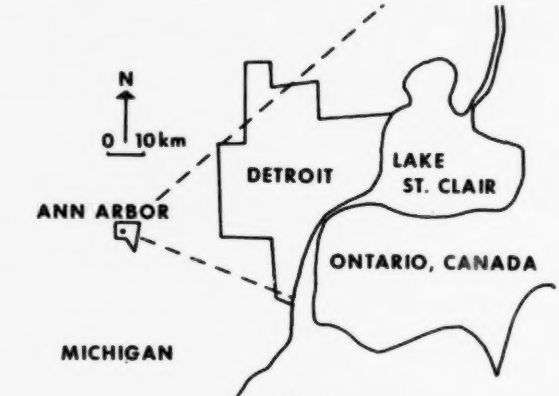
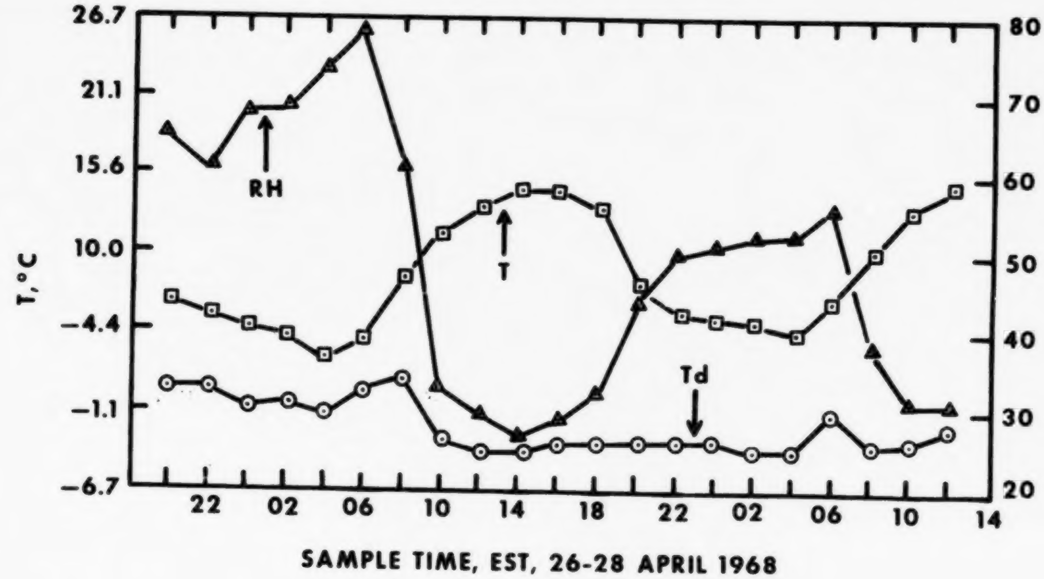

N
0
10km
DETROIT
LAKE ST. CLAIR
ANN ARBOR
ONTARIO, CANADA
MICHIGAN
LAKE ERIE
OHIO

Figure 9. Location of Ann Arbor in relation to Metropolitan Detroit.



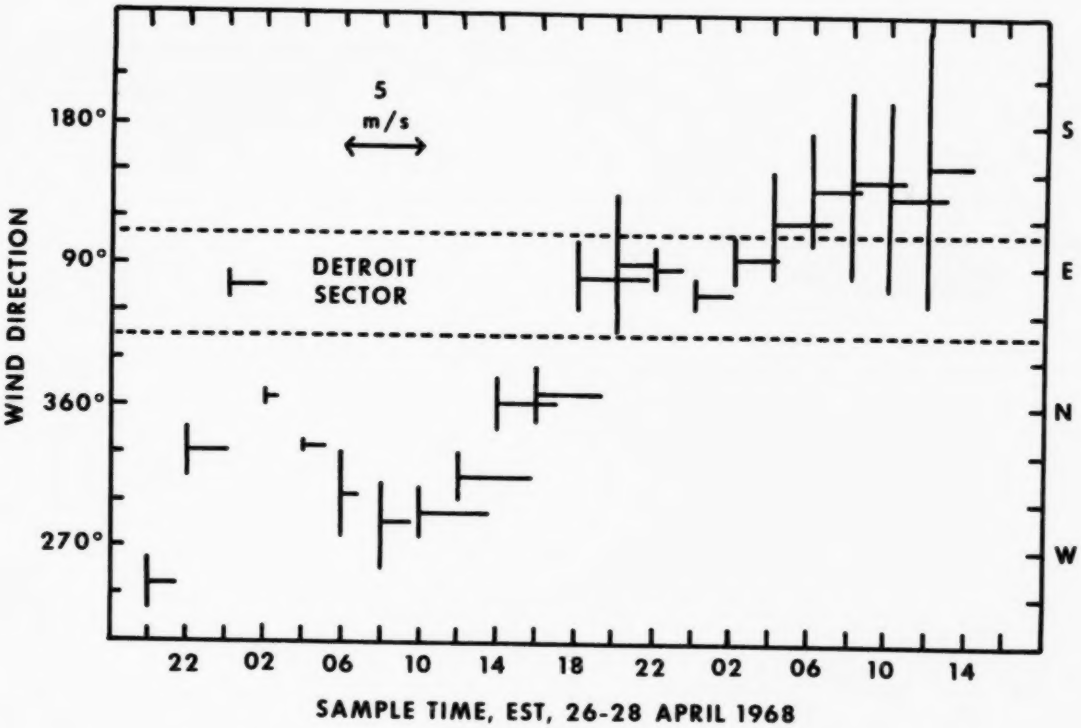


Figure 10. Meterological parameters plotted versus time in 2-hour averages. Width of vertical line for wind direction represents the arithmetic variation in wind direction. The length of the horizontal line represents the average wind speed in meters per second.

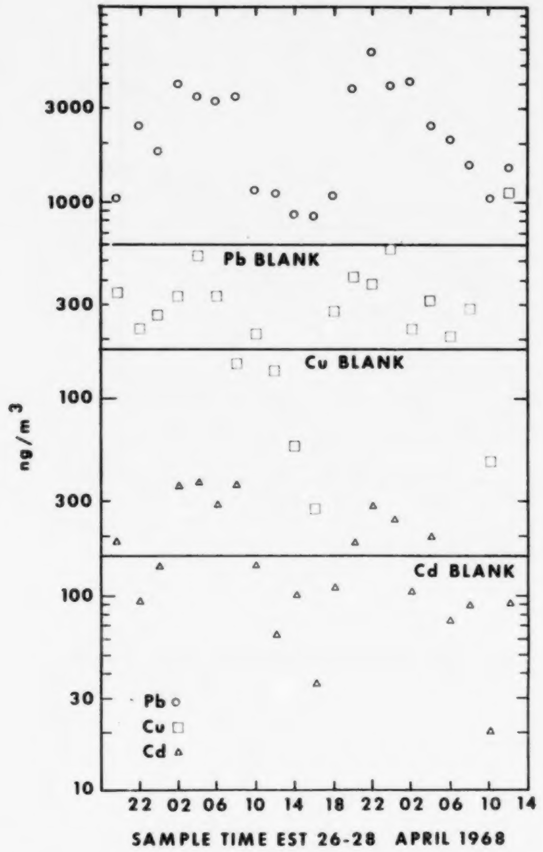


Figure 11. Concentration of lead, copper, and cadmium versus 2-hour time periods. Blank levels represent maximum values of any blank run.

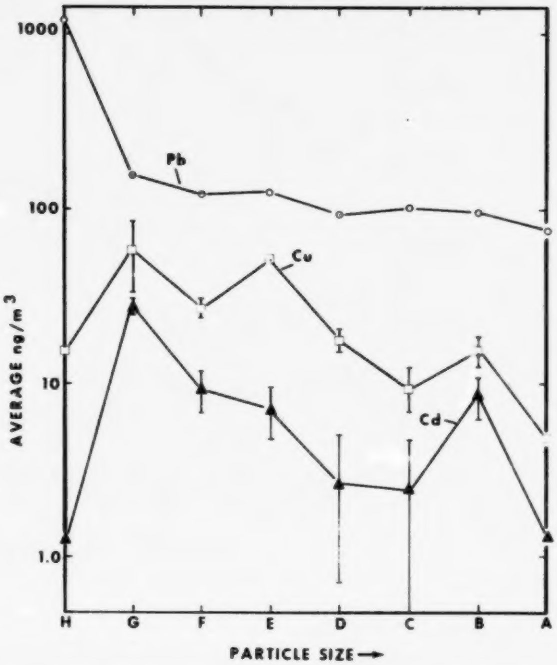


Figure 12. Composite size distribution of the 21 sample runs (2-hour periods). H stage represents a back-up filter to a seven-stage Andersen sampler, mediandiameter 0.5 microns.

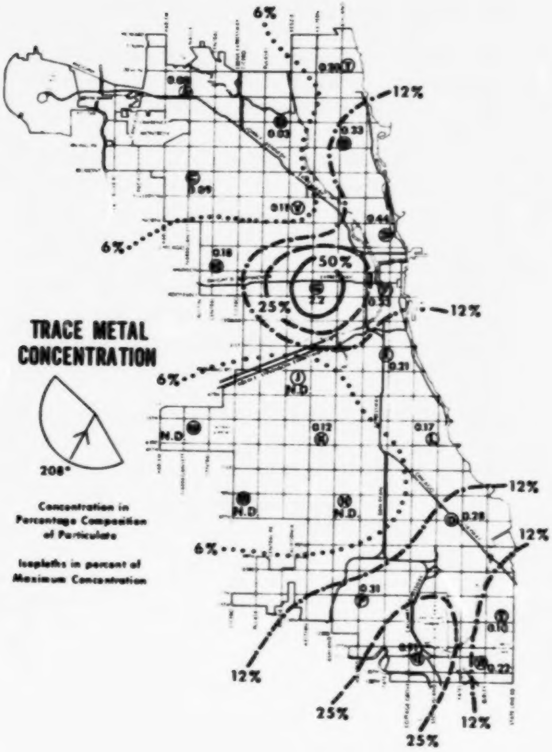

TRACE METAL CONCENTRATION
208°
Concentration in Percentage Composition of Particulate
Isopleths in percent of Maximum Concentration
6%
12%
25%
50%
N.D.

Figure 13. Distribution of zinc, April 11 and June 29, 1971.

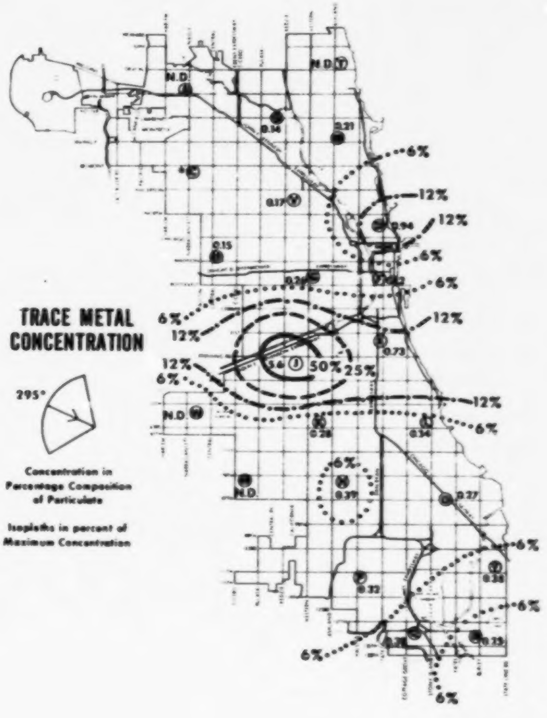

TRACE METAL CONCENTRATION
295°
Concentration in Percentage Composition of Particulate
Isopleths in percent of Maximum Concentration
6%
12%
25%
50%
N.D.

Figure 14. Distribution of zinc, March 7 and 23, 1971.

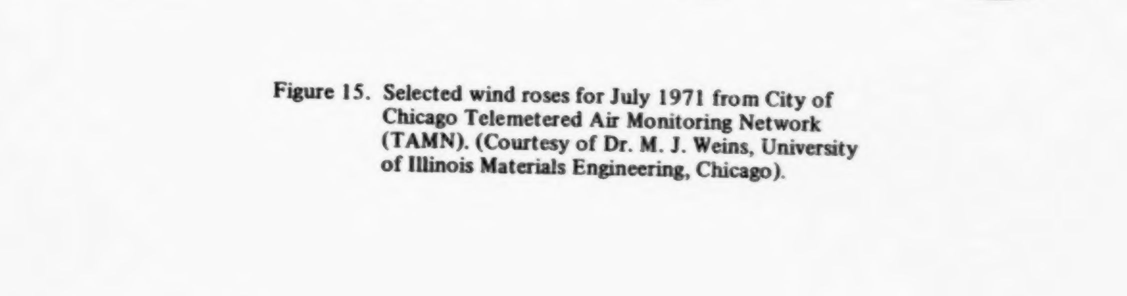


Figure 15. Selected wind roses for July 1971 from City of Chicago Telemetered Air Monitoring Network (TAMN). (Courtesy of Dr. M. J. Weins, University of Illinois Materials Engineering, Chicago).

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MONITORING FOR TRACE METALS – WATER ENVIRONMENT

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MONITORING

Monitoring for metals in the aquatic environment may be described as (a) the location of significant sources of metals discharged to surface waters, the characterization of these discharges as to specific metals, their concentration and physical state, (b) the immediate impact of these discharges on receiving water quality, and (c) the broad evaluation of the concentration of metals in the aquatic environment, including natural background and measurable changes due to human activity.

These types of monitoring may be classified as:

1. Source Monitoring – resulting from the mining, refining, and manufacturing use of metals.
2. Near-Source Monitoring – in the immediate vicinity of the discharge, to determine localized effects.
3. Ambient Monitoring – baseline data collection to assess long-term changes and general levels of metals.

SOURCE MONITORING

Responsibility for monitoring metals at the source is divided between the industry which creates the discharge and the regulating agencies, both state and federal, charged with maintaining satisfactory water quality. The provision of the 1899 Refuse Act requires the permit applicant to identify the metals present in his waste and to report the maximum concentrations present at any time (1). The Standard Industrial Classification categories reporting are listed in Table 1.

Implementation of the new amendments to the Federal Water Pollution Control Act will similarly require monitoring data on metals in industrial effluents. Routine examination of effluents will be needed to evaluate the efficiency of treatment and control measures.

State regulatory agencies, in cooperation with EPA, are conducting source sampling to determine compliance with permit applications. These monitoring activities will be expanded under the new effluent guidelines and standards. Where violations occur, EPA is involved in case preparation, i.e., gathering source data in support of 180-day notices or other legal actions.

TABLE 1 HEAVY METAL REPORTING REQUIREMENTS

SIC classification	Industry
10-14	Mining
22	Textile Mill Products
2491	Wood Preserving
26	Paper and Allied Products
281	Industrial Inorganic and Organic Chemicals
2818	Industrial Organic Chemicals
2819	Nuclear Fuel Reprocessing
283	Drugs
2879	Agricultural Chemicals
2892	Explosives
29	Petroleum Refining
33	Primary Metal Industries
332	Iron and Steel Foundries
333	Primary Smelting and Refining
336	Nonferrous Foundries
34	Fabricated Metal Products
347	Coating, Engraving
36	Electrical Machinery
3731	Ship Building and Repairing
285	Paints, Varnishes, Lacquers, and Enamels

NEAR-SOURCE MONITORING

Collection of metals data in receiving waters establishes the immediate impact of the discharge. At these downstream points concentrations are maximum, since dilution and precipitation at greater distances will reduce the levels significantly. Toxicity effects may be acute in the mixing zone, and transport processes begin in these areas. Evaluation of metals concentrations near the source contributes to the separation of acute from long-term chronic effects. These data are necessary to establish the responsibility for unsatisfactory water quality and to determine requirements for abatement from known sources of contaminants.

The discharge of wastes containing heavy metals often results in the formation of insoluble materials, as the result of reaction with alkaline waters, coprecipitation, or adsorption on clay particles. The familiar yellow boy in streams receiving acid mine drainage is an example of these chemical reactions. In many locations immediately downstream from metals discharges, bottom sediments contain large amounts of metals and may be classified as industrial sludges. Sampling and analysis of the deposited materials give important information on the original source of the metals and are essential to proper evaluation of the impact on the receiving water. These reservoirs of metals may contribute to poor water quality long after the discharge has been eliminated.

Monitoring in the vicinity of waste discharges is primarily the responsibility of the regulating authorities although many industries conduct their own programs to assess impact. The states and EPA carry out surveys and operate long-term stations at points of maximum damage.

AMBIENT MONITORING

Collection of base-line water quality data, or trend monitoring as it is often called, is essential to an understanding of general water quality available for all purposes and for the assessment of degradation or improvement in specific waterway systems. Public agencies, both state and federal, have been conducting such monitoring programs for many years. In 1968 the Federal Water Pollution Control Administration published a summary of trace metals data on samples collected from October 1962 through September 1967 at approximately 130 stations throughout the contiguous United States (2). These data, derived from more than 30,000 separate determinations, indicate that, of the nineteen elements routinely sought, boron, barium, and strontium occurred with a frequency of over 98 percent, while aluminum, lead, chromium, molybdenum, and nickel varied between 16 and 33 percent. Cadmium, beryllium, silver, cobalt, vanadium, and arsenic were detected in less than 7 percent of the samples.

It should be emphasized that these data represent only the metals in solution and that total concentrations of metals, including suspended forms, would be much higher. Concentrations given, therefore, represent only the minimum levels present and, while permissible concentrations established by the USPHS Drinking Water Standards for public water supplies were exceeded in only isolated samples, the levels considered safe for aquatic life were probably exceeded in many locations.

The U. S. Geological Survey has published a survey of more than 720 stations sampled in October and November 1970 (3). The samples were analyzed for arsenic, cadmium, hexavalent chromium, cobalt, lead, mercury, and zinc. As in the FWPCA study, only soluble metals were determined. Twenty-one percent of the samples has arsenic greater than 10 μg/l, 4 percent of the cadmium results exceeded 10 μg/l (the PHS upper limit for drinking water). There were no hexavalent chromium concentrations in excess of 50 μg/l, and few samples contained more than 50 μg/l of lead. In none of the samples did the concentration of dissolved mercury exceed 5 μg/l, while a significant number of samples exceeded the drinking water standard of 5000 μg/l of zinc.

A survey of public drinking water systems conducted by the Public Health Service in 1969 (4) has indicated that 1.6 percent of the supplies exceeded the limit for copper, 8.6 percent exceeded the limit for iron, 8.1 percent exceeded the limit for manganese, and 1.4 percent exceeded the mandatory limit for lead, while standards for the other metals were exceeded by less than 1 percent of the water supplies examined. Considering that only 969 water supplies were tested, some concern for the quality of water reaching the consumer is merited.

All of the above studies show a problem of metals in the aquatic environment, but the problem may be more acute than realized since limitations of sampling and analysis may hide significant factors of toxicity.

DATA STORAGE AND RETRIEVAL

Water monitoring data collected by federal and some state agencies is stored in a dedicated computer system operated by EPA. A large amount of information on metals concentrations in surface waters is available from this data bank, which can be accessed by any of the ten regional EPA offices.

MONITORING REQUIREMENTS

A satisfactory monitoring program for metals in the aquatic environment has certain basic requirements. These are proper sampling frequency, control of sample stability, specificity, adequate sensitivity, high degree of accuracy, and satisfactory analytical precision.

Certain industrial operations producing discharge of metals are batch operations, resulting in wide variations in loading and concentration. Depending on the degree of dilution, the downstream receiving waters may show similar peaks requiring adjustment of the sampling frequency to detect these variations.

Heavy metals in many water and waste samples are unstable. Precipitation, adsorption on silt particles and container walls, and changes in valence state may occur soon after sample collection. Standard practice includes acidification with nitric acid at the time of sampling to avoid these changes.

In order to properly characterize the metals present, it is essential that the analytical procedure be very specific for the metal being measured. This specificity includes determination of the physical state of the metal, example, soluble vs. insoluble forms, as well as the valence state of the metal. Iron and chromium are two classic examples of the importance of oxidation in metals testing.

Permissible levels of some metals in surface waters are extremely low, requiring analytical sensitivity in the microgram per liter range. These sensitivity requirements often challenge the skill of the analyst.

Because of the necessity for determining compliance with regulatory standards, a high degree of accuracy and precision, at the low concentrations encountered, are additional requirements placed on the analysis.

AVAILABLE ANALYTICAL METHODS

In the past, metals in aquous solutions were determined by colorimetric procedures. While adequate sensitivity can often be obtained by these methods, they tend to be tedious and subject to many interferences. In the dithizone procedures, for example, any or all of 17 other metals act as interference in the measurement of the 18th.

Currently, atomic absorption spectroscopy is the most prevalent method for metals analysis of water and waste samples. A very large number of metals can be measured with these instruments, and when solvent extraction or other concentrating systems are used, sensitivity is adequate for most monitoring purposes. In spite of the versatility and simplicity of the instrument, two limitations of atomic absorption should be mentioned. Only one metal may be measured at a time, so that rapid screening to characterize the metal content of the sample is very time consuming, and secondly, only total metal concentration is determined, since the flame reduces all forms of the metal to the atomic species. In spite of these limitations the advantages of AA make it the method of choice in most laboratories (5). Recently a number of procedures have been developed using the cold vapor atomic absorption technique. The determinations of mercury is the best known example of this type of procedure. The familiar Hatch and Ott method for mercury is based on the absorption by mercury vapor in the ultra-violet range of the spectrum (6). Arsenic and selenium can also be measured in this manner, although the methods are not yet widely used. It is likely that other metals may be determined by flameless atomic absorption when the analytical methods are worked out.

Atomic fluorescence, another variation of the instrumental approach, shows promise of success for certain metals not susceptible to measurement by standard AA technique.

Emission spectroscopy overcomes the single-element limitation of AA, since most emissions instruments can be programmed to measure 20 to 30 elements simultaneously on the same sample (7). This approach offers excellent possibilities for screening samples to determine the presence or absence of specific metals. As in the case of AA, extraction or concentration of the sample provides the needed sensitivity for most purposes. However, the total metal concentration, without oxidation state information, is produced by the emission instruments.

Electrochemical methods, particularly polarography, have long been used for the determination of heavy metals (8). Before the advent of atomic absorption, polarography was considered a preferable substitute for colorimetric methods. The technique, however, did not gain the wide acceptance enjoyed in Europe, and the newer and simpler AA method has relegated conventional polarography to only a few laboratories. Recently, however, the anodic stripping polarograph is being seriously considered as a means of measuring certain metals (9). As with conventional polarography, the oxidation state of the metal can be readily determined, and the accumulation of metal on the cathode permits excellent sensitivity. Commercial instruments are now available which provide good accuracy and precision, without the analytical expertise often considered necessary for conventional polarography.

A number of ion-selective electrodes have been developed for specific metals. In general, the electrode approach does not provide the necessary sensitivity for monitoring purposes and these systems are largely used to measure metals in concentrated solutions. Improvements in sensitivity and selectivity might make the electrodes suitable for continuous monitoring situations.

A number of other instruments have been proposed and are being used for the determination of metals. Among these techniques are neutron activitation, mass spectrometry, microwave plasma, X-ray fluorescence, and others. The necessity for relatively complex instruments, sophisticated data reduction systems, and highly skilled operators tend to make these methods unsuitable for routine analysis of a large number of samples. While each has its enthusiastic proponents, these instruments have not gained with acceptance at this time.

QUALITY CONTROL

In any monitoring program the quality of the data collected is extremely important. The significance of the decisions made from the data requires that all analytical results be as accurate as possible, within the constraints of workload, available methods, and economy. The only way to define and control the reliability of laboratory results is through a well designed operational quality assurance program (10). Such a program must include the use of approved methods, the availability of suitable equipment and instrumentation, the use of daily controls on analyst performance, and proper data handling systems. The National Environmental Research Center, through its Analytical Quality Control Laboratory, regularly conducts round-robin studies to establish the precision and accuracy of the methods used by EPA laboratories. At the present time a study to evaluate atomic absorption methods for ten metals is being carried out by more than 100 participating laboratories in EPA, the states, universities, and private industry. The samples used in the study are prepared to exact concentrations of each metal, covering the range of expected levels in ambient waters and industrial effluents. The final report, which will be available to the public, will describe the standard deviation and bias of each method, as well as the range and coefficient of variation of the reported results.

In addition to conducting method studies, the AQC Laboratory makes available a series of standard reference samples for a variety of environmental monitoring parameters, including heavy metals. These samples, available without charge, can be used to evaluate analytical methods, instrument, and analyst performance, and can be used for intra-laboratory quality control.

SUMMARY

Monitoring for trace metals in the aquatic environment involves source and near-source sampling, as well as ambient monitoring for baseline data and trend analysis. Data from studies by EPA and the Geological Survey indicate that significant concentrations of heavy metals exist in some locations, requiring abatement of discharges. A number of satisfactory analytical methods are available and in use to determine metals in water and waste samples. Good Laboratory quality is essential to the monitoring program, and various manuals and reference samples are available from EPA to assist in establishing and maintaining efficient laboratory operations.

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MONITORING OF SOLID WASTES

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Monitoring, as defined by the American College Dictionary, is "something that serves to remind or give warning." As applied to solid wastes, monitoring may be used to identify the quality and/or composition of the wastes.

This might be expected to assess the resource potential of the waste, its energy content, or the content of material which might be recovered for recycling. Such assessment would allow selection of the most suitable method for solid waste processing and disposal.

The solid waste stream reflects all the substances that are in use by the population from which it is derived. In that sense then it can contain anything that can be thrown away. Substances which pose hazards to the environment and to the solid waste worker are included in this material. Proper monitoring would lead to better knowledge of these potential hazards and provide for better control. Hazardous materials, generally speaking, are in small quantities at any given time and are sequestered in a large amount of other materials which make up the majority of the refuse composition (1) (paper 55 percent, metal 9 percent, glass 9 percent, plastics 1 percent, food 14 percent, other 12 percent). In this form they are most difficult to detect. Certain types of hazardous materials may pose a danger to the solid waste worker either during collection or at the processing or disposal site (example, flammable or explosive substances). Ideally a monitoring system should be devised to detect such materials. From a practical standpoint they constitute such a small number of instances and amounts that they rightly or wrongly are relegated to the classification of a calculated risk. (It might be stated that most hazardous materials such as explosives are prohibited from being deposited in the refuse by local ordinances governing the collection and storage of refuse.)

There is another area of monitoring, that involved with solid waste disposal, where the presence of small amounts of various substances can have an adverse effect on the quality of the environment, particularly that adjacent to the disposal site. Monitoring of the discharges of a disposal facility are an example of this problem.

The type of data needed is relative to the way in which the information is to be used. For the most efficient control of energy recovery systems (incinerators), the calorific content, moisture content, ash and noncombustible content are required. For the recycling of metals and other materials it is necessary to measure the quantity contained of the various fractions to be recovered.

Monitoring for trace metals or materials deemed to be hazardous or toxic would of necessity be quite selective since it is necessary to pick out small amounts of such substances in a large mass of material. The possibility of hazardous material appearing at any time makes the monitoring continuous. It would generally be considered adequate to detect the presence (yes or no) rather than the amount or quantity of a hazardous material.

The format of the information has to reflect the manner in which it will be used. Continuous readout data would be helpful in monitoring the material to be fed to a continuously fed incinerator, since the operation of the furnace requires response to its fuel supply.

The format needed for evaluation of material for recycling would not need to be continuous. It could be intermittent, more to determine the potential, initially, and later to determine if the recovery operation was as effective as it was intended to be.

Accuracy requirements of a monitoring system vary but in no case is it essential to be extremely accurate. Combustibility or calorific content within 10 percent, plus or minus, moisture within 5 percent, plus or minus, are more than adequate for the control of an incinerator based on fuel input. Measuring the metal content for evaluating recycling potential or efficiency would depend on how good the separation process was expected to be and the accuracy of evaluation scaled accordingly.

The accuracy required in monitoring the discharges from a disposal site would probably be more precise in that they would have to detect smaller quantities of materials which involve more sophisticated analytical processes. (In the final analysis this type of monitoring is actually easier than many of the others.) The accuracy as a percentage would be adequate to plus or minus 10 percent in most cases. The frequency of measurement would need to be often enough to detect a significant change in effluent quality so that corrective measures could be taken in time to prevent any serious impact on the environment. This varies with the type of possible pollutant and its form. Gases, for example, would be monitored very frequently, if not continuously, whereas ground water quality could be done much less often.

As to where monitoring is to be done, it should reflect the need to respond to the results obtained. If the determination is to be the basis of decision as to collection and/or storage and perhaps recycling of selected components, the monitoring would be done (a) at the source (example, industry or residence) where different modes of separation, storage or containerization might be required, or (b) at the process point (processing plant, landfill or incinerator) so that changes could be made as necessary in methods of operation. If monitoring of environmental quality by detecting the possible effects of leachate or air pollution derived from a disposal facility is desired, then the disposal site itself or the area immediately adjacent should be selected.

Monitoring techniques now in use vary rather widely. With a few exceptions they are more qualitative than quantitative. Most of the information obtained to date has been as the result of the manual partioning of representative samples of solid waste taken at the various points described earlier. The selection of categories into which the waste was divided being determined by the uses to which the data were to be put.

Britton (2) has stated that a minimum size sample of 300 pound is needed for most studies of a general nature. It was shown in this same study that a minimum of 10, 300 pound samples is necessary from 500 tons of waste to maintain a confidence interval of 90 percent. (In measuring constituents by this method, very little if any effort has been expended in measuring trace elements, only the metals present in relatively large quantities being reported. All others were grouped as other or miscellaneous.)

Monitoring techniques for measuring metals and other constituents of leachate, which may develop from landfills, are being used in conjunction with observation wells and lysimeters constructed in the areas immediately adjacent and beneath the landfill. In general these consist of some sort of sampling equipment for taking intermittent samples for analysis by chromatographic or other techniques. These techniques are reasonably successful in measuring the changes which occur in ground water adjacent to disposal sites and the effectiveness of sealants and other measures to reduce or eliminate leaching conditions. They are expensive to install, maintain, and operate, especially considering the length of time needed for monitoring in some instances. Metallic ions such as iron, zinc, nickel, copper, and sodium can be determined (3).

Equipment for monitoring of stack gases from incinerators on a continuous basis is available but is usually limited to particulate determinations. This equipment is expensive to install, maintain, and operate and its reliability leaves something to be desired. Trace metals can be detected in samples of dust but are not usually analyzed routinely since air pollution codes are at present concerned only with particulates per se. If and when codes become more stringent with respect to gaseous and other constitutents, more sophisticated analysis will be used and trace metals may be included. In some special industrial situations where hazardous conditions exist (lead, mercury, etc.), these metals are monitored routinely.

Continuous monitoring of solid wastes is a most difficult task due to its variations in shape, composition, and complexity. Several methods are in use and others are under study and in various stages of development for detecting and segregating various components from a continuously moving stream of solid wastes. (It is usually necessary to pre-process the waste by shredding or grinding in some manner to produce a more uniform particle size and to expose more of the waste.)

Magnetic separation of ferrous metals from the rest of the waste has been in use for many years. This method is relatively successful if the metal is accessible, and a certain amount of entrapped and attached extraneous material is acceptable (in the case of raw refuse). Metal can be separated from incinerator residues without much more treatment than tumbling over a coarse screen. Rather complete separation of nonferrous metals can be accomplished from certain types of waste (example, residues from shredding automobile bodies) after removal of ferrous metal magnetically. Other materials are separated by such means as air classification, heavy media flotation and differential melting of lower temperature melting point metals (4). In this process zinc, aluminum, stainless steel, red metal, and steel are separated on a continuous basis. Rubber and glass are by-products which can be segregated if a market is available. To date no trace metals are segregated by this process. If present they are considered as impurities in the other metals.

There are several methods other than magnetic for segregation and monitoring solid wastes on a continuous basis under consideration and development. Material might be monitored on the basis of its bulk density, optical characteristics, fiber content, eddy-current reaction, and impact characteristics to name a few.

Mechanical methods of monitoring on a continuous basis are essential if the many idealized objectives described earlier are to be accomplished. Unfortunately each of the proposed systems have much to be done to them before they will be ready for practical application (5).

There is no practical continuous method available at present for determining such characteristics as the ~~moisture content~~ of a heterogeneous mass such as refuse. The infra red scanning technique for example can only at present measure the character of the surface and is complicated by the presence of metals. The measurement of the calorific content is very slow and cumbersome by present methods and there seems little likelihood of being able to improve the situation. No continuous method of evaluation is available. Alternatives to continuous monitoring for incinerator operation might consist of separation of the noncombustibles prior to some form of continuous moisture determination which when coupled with statistically rigorous information from prior testing could be used to indicate the combustibility of the material for control purposes.

Detection of trace metals in the refuse stream on a continuous basis seems to be highly unlikely when viewed from the present situation. If complete processing were considered which includes a reliable and efficient means of reducing the refuse to a uniform particle size, and a reliable high velocity automatic sorting device was available to separate the constituents, then monitoring for the presence of trace metals as well as other metals might be possible.

Several separation techniques have been developed and are in various stages of application. The hydropulper process separates fiber and performs several other sorting operations resulting, among others, in a metal-glass effluent which is further sorted optically. Air classification, sorting by conductivity, photometric methods, sorting by "bounce" are some of the several methods besides the magnetic separation discussed earlier which are being evaluated by various agencies and individuals. In the main, these various methods need testing and improving before they can be considered able to handle economically and continuously such diversified wastes as municipal refuse. There is every reason to expect that the sorting techniques will be improved and problems ironed out so that adequate separation can be accomplished in the future.

Most monitoring of waste streams today are done visually with adjustments being based on judgment and experience. If an object is noted which should be removed it may be taken out by hand. Hand sorting of metal is still common in many salvage operations where the value of the material is great enough to pay for its removal. Visual monitoring of wastes at the disposal sites (example, sanitary landfill) may indicate that the material needs special handling to avoid difficulty in the operation.

The laboratory techniques used to analyze the samples taken from monitoring stations at landfills or at incinerators as well as the setting up and operation of the sampling equipment require a certain amount of training and ability. Personnel who are assigned sampling and analytical responsibility should be adequately trained to carry out these tasks so that the results can be depended upon. This type of training is somewhat specialized and would require knowledge of basic chemical laboratory technique and sampling procedures. Such training can be obtained in several ways, ranging from formal college training to short courses specially taught thru some governmental agency.

In general monitoring has been conducted only when required by some regulatory agency in order to assure compliance with a regulation or environmental quality criteria. The exceptions are those facilities where research or demonstration projects are being conducted to determine the effects of some operation. Under these circumstances monitoring can be done by the waste producer to assure, for instance, that no hazardous materials enter the solid waste stream. This could apply equally well to householders and to industry. The level of monitoring would vary widely from one extreme to the other. This would be monitoring prior to collection of the waste while it is still at the point of generation. Monitoring at the point of processing or disposal is more likely to be done by the agency operating that facility especially if the information is to be used to modify the operation of the facility. If environmental quality is the reason for monitoring, then the operator of the facility may be responsible for the monitoring or it may be done directly by the regulatory agency itself.

The data gathered certainly will be useful locally. Its wider spread usefulness may consist more of indicating trends and variations from place to place and to indicate effectiveness of various treatment and monitoring methods. Such trends and variations would likely be of interest to a state or federal agency, especially those involved with environmental quality.

If the generator of the waste is the one who benefits from the information gained by monitoring of his solid wastes, then obviously he should bear the cost. If it is necessary to monitor the wastes on his premises to protect his employees or the environment, then he should also bear the cost as a part of his costs of doing business. Since the collector of the wastes in some cases serves as an employee then he can expect some protection as well from the monitoring of the wastes he picks up.

The disposer or processor of the waste may be responsible for payment for monitoring if he is the beneficiary of the information as in controlling his operation. He may also be required to provide information supporting his position in protecting the environment in which case he will have to pay for the installation, sampling, and testing required in the monitoring system. If the monitoring is being done to protect the environment, then the regulatory agency responsible for environmental control in the area must maintain surveillance and monitoring equipment of its own in order to assure that protection is being provided. The costs of such operation would most likely be paid for by the regulatory agency from public funds. There have been instances where those being regulated were expected to pay for such monitoring. In any situation involving interstate jurisdiction a federal agency would probably be involved. In this case the U.S. Environmental Protection Agency would be expected to monitor the local agencies' operations and would serve as a collection and distribution medium for data and information of value to other states and agencies.

SUMMARY

In summary it can be said that at present the monitoring of solid wastes in general is far from adequate and for trace metals is hardly considered. More must be learned of the importance of trace metals from solid wastes upon the quality of the environment. Studies to date have not indicated that trace metals are a problem from this source (6), but more work needs to be done.

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MONITORING FOR TRACE METALS IN FOOD

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INTRODUCTION

Monitoring for trace metals in foods poses problems of much greater scope and complexity than casual consideration might suggest. It is the purpose of this paper to at least delineate these problems and to indicate progress in their control. The privilege of giving the presentation on this subject of major significance to the Food and Drug Administration's area of responsibilities is sincerely appreciated. This report will deal with the past and current situations and the business ahead, with particular emphasis on the analytical aspects of the subject. Although this seems an excessively ambitious coverage in the brief space available, an understanding of the subject problem as it has challenged the Food and Drug Administration requires at least some such approach to develop an understanding of the analytical and surveillance situations as of today.

This presentation will be restricted primarily to the analytical problems and surveillance activities of FDA in this field, but these problems are quite common to other agencies responsible for control of toxic metal contaminants in foods and, accordingly, should suffice to illustrate the general situation.

Aside from the sporadic incidents which are always upsetting our well-laid plans, the primary problems in contamination of foods by toxic metal residues recognized prior to World War II were associated with use of insecticides containing copper, mercury, arsenic, and/or lead. Development of methods, surveillance, and regulatory programs constituted major efforts of the Food and Drug Administration and of the responsible state and local regulatory agencies. For example, during the apple harvest season the entire inspectional and analytical staffs of FDA field stations in primary growing areas were engaged in surveillance of apples for lead arsenate residues. Cases of apples awaiting analysis were then stacked from floor to ceiling at the FDA Cincinnati Laboratory where I worked. Similarly, primary resources of field stations in other major crop areas were assigned to surveillance for residues of lead arsenate and of the other metal-based insecticides then prevalent. At that time a major proportion of the staff at the Washington Headquarters' Division of Food was engaged in research to improve the sensitivity, accuracy, and reliability of analytical methods for the determination of such residues. The enormous growth in the use of organic pesticides following World War II posed new much more complex residue problems. The consequent major displacement of the conventional metal-based agricultural poisons led to the virtual discontinuance of research on determination of toxic metals in foods, and resulting loss over the years in the food laboratories of resources, both personnel and equipment, adapted to trace heavy metal analysis. However, the occasional diversion of surplus seed wheat treated with mercurial fungicides into the commercial wheat supply stimulated attempts to determine trace levels of mercury above background. The FDA (1) published the technique for measurement of mercury by cold vapor flow absorption cell as early as 1966. Its adaptation to determination of submicrogram quantities of mercury in wheat, fish, and eggs (2, 3) gave initial successful results with a sensitivity of 0.01 ppm. However, the subsequent inability to acquire reagents sufficiently free of mercury and the very low levels found in the samples initially analyzed (0.01 to 0.03 ppm) discouraged continuance of the research. Nevertheless as early as 1967, FDA checked the mercury content of a number of total diet categories by neutron activation analysis (4), finding values of the same order as those cited above. It is interesting to speculate if the mercury contamination problem in fish might not have been discovered earlier if the stringent sensitivity requirement for the specific wheat problem had not discouraged further analytical research on mercury at FDA.

The approach to food supply surveillance, the FDA total diet or market basket survey, originated for radionuclide surveillance (primarily ^{90}Sr) was adapted and proved effective for pesticide residue monitoring, and has now been expanded for use again as one means of surveillance for toxic metals. It is manifestly impossible to ensure freedom from toxic residues of every lot of every product in a food supply as enormous and as diversified in kind, source, processing, packaging, and distribution as that of the United States. The most effective surveillance for overall safety which practicable resources can provide is periodic examination of a representative total diet for potential toxic residues, complemented by analysis of specific commodities in which occurrence of particular residues is most probable. The concept and use of total diet or market basket surveillance have been described in detail (5). It will suffice here to summarize this FDA program currently as periodic collection and analysis, as prepared for consumption, of twelve composited food categories representative of the two-week diet of a 15 to 20 year old male for the northeastern, southeastern, central and western regions of the United States.

At this point, it seems appropriate to emphasize that the brunt of the surveillance and monitoring work is borne by the District Laboratories of the FDA. The function in the Division of Chemistry and Physics, Bureau of Foods, is primarily to undertake necessary analytical evaluation and/or development work in support of surveillance operations and to provide highly specialized and sophisticated analytical support services, such as neutron activation analysis. It should be emphasized that the district laboratories also contribute to the analytical research and evaluation, both through original work and through conduct of and participation in collaborative studies. These district functions are greatly facilitated by the advice of competent outside scientists assigned to each district laboratory as consultants.

THE CURRENT SITUATION

As is well known, the sudden resurgence of the problem of toxic metals in foods arose with the Minamata incident in Japan and the findings of high levels of mercury in fish in Sweden and in Lake St. Clair, Canada. There was an immediate need for analytical methods applicable to determination of inorganic mercury and of the more toxic methylmercury found in Sweden to be the predominant form of occurrence in fish. Cold vapor or flameless atomic absorption is most commonly used for total mercury determination, while the Westöö procedure (6) appears quite reliable for determination of methylmercury. An international collaborative study (sponsored by the Society for Analytical Chemistry and the AOAC) is in progress and should establish the degree of reliability of the various mercury methods involved. A comprehensive report on surveys of mercury in fish and other foods was presented at the recent meeting of the AOAC by Simpson and Horwitz (7). I shall summarize that presentation briefly. It involves typical application of the combined approaches of total diet and individual commodity surveillance. It also exemplifies the analytical problems in trace metal monitoring of the food supply and in evaluation of the toxicological effects. The survey of canned tuna was undertaken by FDA in cooperation with the National Canners Association and the National Oceanographic and Atmospheric Administration. The results showed that about 4 percent of the more than 2000 samples examined exceeded the FDA action guideline of 0.5 ppm, the average being 0.25 ppm. It was also shown that the larger the fish the higher was the average mercury level and the proportion exceeding the guideline. A similar observation was made with respect to Pacific halibut by the National Marine Fisheries Service.

FDA undertook a survey of swordfish as well as of 19 other species of commercial fish and shellfish. The extensive findings 95 percent of high levels of mercury in swordfish exceeding the action guideline of 0.5 ppm necessitated the FDA ban on swordfish distribution (Table 1). In contrast, of the 19 other species surveyed (Table 2), only 4 (bonita, cod, mackerel, and snapper) showed a significant percentage exceeding the guideline (Table 3). In these cases the analytical method employed was the cold vapor atomic absorption method of the Fisheries Research Board of Canada or a similar procedure (8). In addition, in cooperation with 45 states, the Tennessee Valley Authority, and the Environmental Protection Agency, surveys of fish from fresh water fishing areas throughout the Unites States were completed. About 40 percent of all samples examined exceeded the 0.5 ppm guideline. Closure of fishing areas and/or warnings against eating fish taken from polluted waters were issued by 16 of the states covered in the survey. Import samples of freshwater species showed about the same proportion (45 percent) containing excessive mercury.

TABLE 1 DISTRIBUTION OF Hg LEVELS IN SWORDFISH ABOVE 0.5 ppm GUIDELINE

ppm Hg found	% of total samples
0.50–0.74	13.7
0.75–0.99	33.2
1.00–1.24	26.5
1.25–1.49	15.3
1.50–1.99	8.5
2.00–2.99	2.4
≥ 3.00	0.3

TABLE 2 SEAFOOD ANALYZED FOR Hg

Bonita
Clams
Cod
Crab
Flounder
Haddock
Hake
Halibut
Herring
Lobster
Mackerel
Oysters
Perch
Salmon
Sardines
Scallops
Snapper
Trout
Whitefish

TABLE 3 SEAFOOD WITH >0.5 ppm Hg

Type	Mean ppm	%> .5 ppm
Bonita	0.30	10
Cod	0.09	3
Mackerel	0.12	3
Snapper	0.31	18

TABLE 4 NAA FOR MERCURY IN FOODSTUFFS (ppb)

Commodity	No. samples	Median	Range
Flour	28	<3	<3–6
NF Dry milk	33	10	<4–27
Sugar	22	<3	<3–10
Potatoes	33	3	<1–15
Beef	23	3	<2–7
Chicken	24	3	<1–7
Shrimp	32	14	5–43
Beef liver	22	3	<2–8
Eggs	33	<2	<2–5
Whole milk	23	<1	<1–9

A great deal of concern was aroused in both the United States and Canada by a report of a Canadian University scientist, and his associates (9), that as much as 0.3 to 0.4 ppm of mercury occurred in some samples of such staple foods as flour, hamburger, fruits, vegetables, and cocoa. The report gained wide publicity and, though the findings were ultimately shown to be erroneous, stimulated a crash program of mercury surveillance of the food supply in the United States and Canada. Regulatory officials in both countries were startled by findings (9), which were higher by at least an order of magnitude than those found in earlier surveys of like commodities in Canada (10) and the United States (11). The initial report was based on neutron activation analysis (NAA) (9). While the technique is capable of a high degree of sensitivity in conjunction with radiochemical separation of the radioactive mercury, it was not well adapted for the urgent large scale survey indicated as necessary. For this purpose, the flameless atomic absorption technique (8), was utilized as the initial method in a nationwide survey by FDS District Laboratories of the mercury in eight staple food commodities (wheat, flour, nonfat dry milk, fluid whole milk, cane sugar, potatoes, beef, chicken, and eggs) in addition to liver and shrimp, selected as edible concentrators of mercury in the environment. Because of the uncertainty about reliability and sensitivity of the technique, a crash program of neutron activation analysis was instituted at FDA Headquarters on subdivisions of the same samples. No measurable quantities of mercury were found by the atomic absorption technique in any of the commodities, although several samples of shrimp showed indications of mercury at about the limit of measurability, approximately 0.05 ppm. The more sensitive NAA method, a modification (12) of the Jervis procedure, yielded the results in Table 4. It is noteworthy that all values are well within the WHO recommended maximum permissible level of 50 ppb.

It is apropos at this point to discuss the discrepancies of at least an order of magnitude between the FDA results and those reported by Dr. Jervis, both using essentially the same NAA technique. In our initial application of the Jervis technique, extreme variations in replicate results were observed. After much experimentation, it was found that these arose from adventitious contamination by mercury in the laboratory of both the sample itself and of the exterior of the vial in which the sample was irradiated. It was only after handling of the sample was transferred completely to a clean room free of mercury vapor and after rinsing of the irradiated vials in acid before opening that consistent replication and sensitivity of 2 ppb of mercury in dry food were attained. It seems at least likely that the high initial values by NAA that Jervis reported in some Canadian foods are attributable to such contamination. The consistency of NAA analyses by the FDA technique was indicated by comparison with results obtained by other laboratories on a variety of samples including three standard reference materials (12). During the current year, total diet samples have been analyzed for mercury, using both the cold vapor atomic absorption and the NAA techniques. It must be realized that because of the dilution effect of compositing the various product samples in the 12 total diet categories, an order of magnitude better sensitivity is required than that which is adequate for analysis of the individual products. Accordingly, for total diet mercury surveillance, the atomic absorption method can only provide an indication of relatively excessive contamination. It is not adequate to provide the kind of natural background data which our toxicologists very much desire to permit evaluation of the normal total body burden of such toxic metals. Nevertheless, the relative speed and convenience of the method in discovery of possible excessive contamination justifies its continued use in total diet analysis. The results of the 1972 NAA survey of total diet samples (Table 5) further confirms the earlier indications that, with the exception of certain fish, the U. S. diet is essentially free of mercury.

A related responsibility of the Division of Chemistry and Physics is to provide analytical services, if necessary, or recommend applicable analytical procedures in support of our toxicologists' evaluation of the nature of the hazard of metal residues through examination of organs, other tissues, biological fluids, etc. of test

TABLE 5 NAA FOR MERCURY IN TOTAL DIETS

Food item	Mercury conc. (ppb): 1972				
	Balt.	Bos.	K. C.	Minn.	L. A.
Dairy products	<1	<1	<1	3	2
Meat, fish, poultry	30	27*	8*	9	27
Grain, cereal product	3	8*	5	<2	< 2
Potatoes	3	8*	2	3	< 1
Leafy vegetable	5*	5*	3*	<1	< 1
Legume vegetable	<2	<1	<2	<1	< 1
Root vegetable	2	<1	<1	<1	< 1
Garden fruits	2	2	<1	<1	< 1
Fruits	<2	2	3*	<1	< 1

*Avg. values.

animals. A special problem was posed by the desire to study localization of mercury residues in discrete sections of rat brains following ingestion of methylmercury. Only a few milligrams of sample could be supplied, but by utilizing NAA we were able to supply the required data. For the hundreds of blood analyses required, fortunately the rapid Magos procedure (13) has proved reliable.

I have chosen to devote what may seem an excessive proportion of time to the mercury problem. This is, partially, because more information is available on the analytical methodology and on the occurrence of mercury in foods. But more significantly, as indicated earlier, the experience with mercury illustrates the gamut of analytical problems to be anticipated in the monitoring of trace metals.

There is need for practicable methods of adequate sensitivity to monitor individual food commodities; for methods of a sensitivity an order of magnitude better to monitor composite total diet categories of commodities; for methods applicable to determination of the normal background level of the metal in foods; for methods for identification and determination of the various forms in which a toxic metal residue occurs in foods; for practical methods applicable to the often minute samples that are the only ones available in toxicological studies; for automated methods to facilitate analysis of a large number of samples. Necessary to, and perhaps eclipsing, all of the preceding is the need for studies of methods of sample preparation and sample dissolution or reduction to make the products amenable to the ultimate determinative phase without loss of the toxic residue or adventitious contamination of the sample. There is also need to be extremely cautious to avoid arousing undue public alarm and pressure to undo fictitious knots with consequent diversion of limited resources from really critical problems. As we face the broader monitoring problem, it is obvious that we are also in need of reliable multielement methods.

In recognition of the prevasiveness and possible health hazard of many metal residues, FDA toxicologists developed a list of metallic elements posing or potentially posing a problem in groups in an approximate order of decreasing estimated significance (Table 6). It should be pointed out that some elements within a group may be included not in relation to their intrinsic degrees of toxicity but in relation to the effect of their presence on the toxicity of other elements therein; for example, in the first group, zinc is included because of the significance of the zinc-cadmium ratio to the toxicity of cadmium. Beyond these, FDA is concerned with Ni, Co, V, Mn, Mo and up to a total of twenty or more metals occurring in the environment, the forms, concentrations, and toxicological significance of which are virtually unknown. This broad spectrum of metals, in conjunction with the variety of analytical needs cited, has posed a monumental task which neither FDA nor any other organization has adequate resources in personnel and equipment to complete as soon as is desirable. In the face of the urgent need and the lack of enough chemists experienced in trace metal analysis in foods, FDS is undertaking to expedite progress by reassigning a cadre of chemists from other important but lower priority projects to work with those experts available in methods development; soliciting outside contract support both in studies of potential multielement techniques for the metals of primary concern and in evaluation of any existing methodology for metals of secondary concern in application to food analysis; and utilizing, as available, methods recognized as of less than adequate sensitivity, to undertake total diet and individual commodity surveillance in order to avoid repetition of the mercury experience, that is, the failure to discover an existing excessive contamination situation while resources are all devoted to refinement of techniques.

TABLE 6 METALS OF CURRENT CONCERN

GP I	–	Pb,	Hg,	Cd,	As,	Se,	Zn	
GP II	–	Be,	Ge,	Sb,	Tl,	Cu,	Cr,	Sn

A special problem of concern is the hazard due to migration of toxic metals from glazed pottery into food. Primary attention has been given to contamination by lead and cadmium. The test procedure for the leachable metals involves exposure of the vessels to acetic acid and determination of the extracted lead and cadmium by atomic absorption spectrometry. A field surveillance program has revealed few instances where domestic products have exceeded the interim action guidelines of 7 ppm leachable lead and of 0.5 ppm leachable cadmium, but these have been exceeded by a significant proportion of imported pottery. A limited survey of cadmium leachable from enamelware again has revealed no problem with domestic products, but about one-third of the imports exceeded the interim guideline during the past year.

Another problem of special concern has been occurrence in evaporated milk of higher than tolerable levels of lead. This is, of course, a matter of particular significance because of its extensive use in infant formulas and because of evidence that young children absorb and retain lead more readily than do adults. In order to evolve a reliable method for the determination of lead in evaporated milk, FDA in cooperation with industry laboratories undertook a collaborative study of an atomic absorption and of an anodic stripping voltammetric procedure (14). The results by atomic absorption at levels of 0.16 ppm and above, including the range of special interest up to 0.27 ppm, were quite satisfactory. Insufficient results have been received for evaluation of the electrochemical method, but preliminary results indicate it may prove superior at levels below 0.16 ppm. Meanwhile, the industry has made much progress in modifying can closure solders to reduce the contamination.

In addition to the cited mercury determination using flameless atomic absorption spectrometry (8), the following analytical procedures have been collaboratively studied and adopted as Official, First Action by the AOAC in 1971 and 1972:

Lead in evaporated milk (14)
Lead in fish (15)
Lead in plant and animal products (16)
Lead and cadmium leached from glazed ceramic surfaces (17)
Cadmium in foods (18)

Meanwhile FDA studies are in progress on multielement methods for mercury, arsenic, and selenium in total diet samples by NAA; on mercury, arsenic, selenium, cadmium, and lead in individual commodities by atomic absorption spectrometry; or lead, zinc, cadmium, tin, and copper in commodities by anodic stripping voltammetry; and on cadmium, zinc, and copper in toxicological samples (ppb range) by atomic absorption spectrometry utilizing the heated graphite atomizer accessory.

In conjunction with contract work to extend and expedite coverage of the problem on the metals of current concern, a preliminary limited service contract has issued for study the applicability to food analysis, for some twelve or more metals, of the technique of radio frequency-induced plasma excitation emission spectrometry. Depending on the results of that study, it is being recommended by the Office of Science that a full-scale contract proposal be solicited for such work. Similar recommendations are being made for study of the applicability to food and biological materials of existing methodology for beryllium, germanium, antimony, thallium, copper, tin, and chromium. The objective is to select the best immediately available procedures for use in initial surveillance and for further refinement as necessary.

During the current fiscal year surveillance programs will be instituted on mercury, lead, and cadmium in fish; on cadmium in a variety of foods; and on mercury, arsenic, selenium, lead, cadmium, and zinc in total diet samples. Although the current procedures for the total diet analysis are not of the ultimate sensitivity required, the program will serve to disclose any serious contamination problems.

THE BUSINESS AHEAD

It is apparent from the foregoing that a most formidable task still faces us in the development of methodology and an even greater one in respect to the chronic toxicity and interactions of the less familiar metals. The relationship between the analytical requirements and the toxicological needs seems inevitably to end up in the old chicken-or-the-egg conundrum. The chemist asks what analytical sensitivity the toxicologist requires and the latter asks how much of the metal is there? Fortunately, the advent of the National Center for Toxicological Research will greatly expedite the setting of the goals which the analytical chemist must achieve. During the next fiscal year we anticipate that we should be able to develop enough surveillance data to disclose any patently significant unrecognized contamination of the food supply by the metals listed in Groups I and II above. If fiscal year 1973 contract resources exceed our anticipated minimum it should be possible to similarly deal with all of the twenty or so metals of potential concern.

The special problems must engage our attention very soon. One is a large scale survey of the diet of inner city children for lead, to permit evaluation of the significance to the elevated lead levels in their blood of dietary intake in relation to known adventitious sources (automobile emissions, lead paints, lead water pipes). Another problem relates to the significance to the diet contamination of the use of sewage sludge as fertilizer in growing crops and forage. A preliminary investigation of such use in the Chicago Sanitary District revealed that soybeans so cultivated contained up to 1 ppm of cadmium. It is apparent that a survey of the extent and consequences of that agricultural practice is essential.

How short a time it seems since analytical chemistry, and particularly elemental analysis, was being relegated to that class of routine operations offering no more creative challenge! Only now are we beginning to appreciate that we didn't know enough about the problems to even recognize them and that seemingly inert and innocuous substances can be facilely converted in the biosphere to potent hazards.

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DIMENSIONS OF MONITORING

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INTRODUCTION

The purpose of this presentation is to ask questions, not to provide answers. Our hope is that by the presentation of half-baked ideas we can stimulate the thinking of the scientific community toward an improved view of the environmental monitoring process.

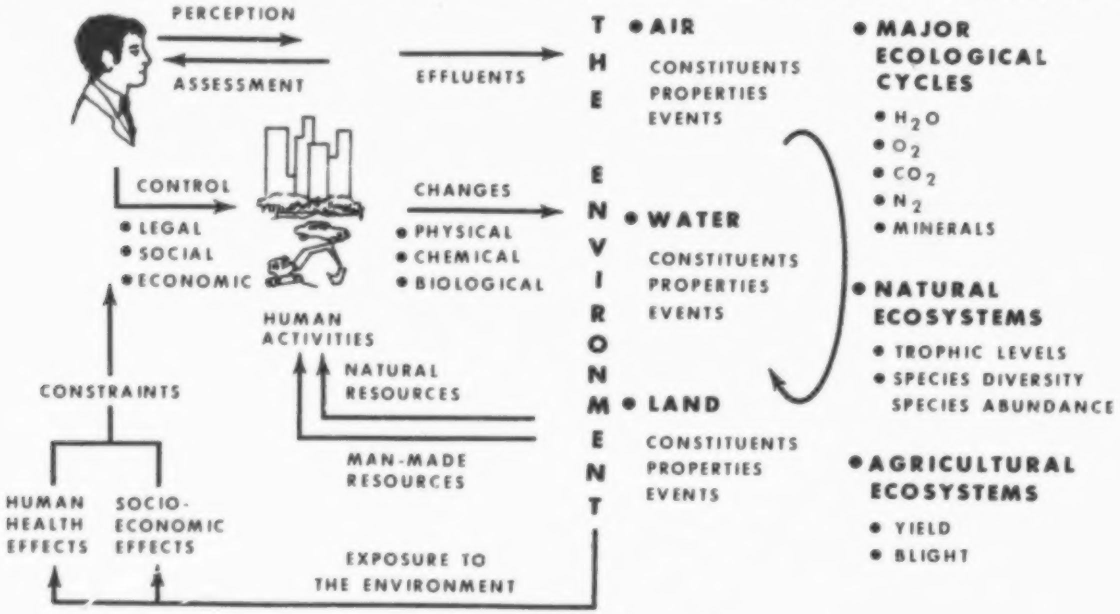
This will be a study of an extreme and a technical caricature. We intend to pollute your mind. What follows will be a series of random snapshots relevant to the concept of monitoring the environment of our nation.

A guiding principle and a pervasive note throughout this presentation is the following. Monitoring networks yield vast amounts of raw data which must be transformed into usable information by a filtering process which generally involves a complex transfer function. This is of paramount importance since monitoring systems exist in support of the decision making process for recommending actions. This process feeds on information not data. For monitoring networks to provide the pertinent information, we must adopt a systems approach in designing these networks.

THE ENVIRONMENT SYSTEM

One often hears that no systematic approach is applied to the solution of our ever-changing environmental problems. This lack of systems approach might result from the fact that we are dealing with a complex system which often follows no clearly predictable pattern.

As illustrated in Figure 1, the total environment includes all conceivable attributes and interactions in the


PERCEPTION
ASSESSMENT
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• LEGAL
• SOCIAL
• ECONOMIC
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• PHYSICAL
• CHEMICAL
• BIOLOGICAL
HUMAN ACTIVITIES
NATURAL RESOURCES
MAN-MADE RESOURCES
CONSTRAINTS
HUMAN HEALTH EFFECTS
SOCIO-ECONOMIC EFFECTS
EXPOSURE TO THE ENVIRONMENT
THE ENVIRONMENT
• AIR
CONSTITUENTS
PROPERTIES
EVENTS
• WATER
CONSTITUENTS
PROPERTIES
EVENTS
• LAND
CONSTITUENTS
PROPERTIES
EVENTS
• MAJOR ECOLOGICAL CYCLES
• H_2O
• O_2
• CO_2
• N_2
• MINERALS
• NATURAL ECOSYSTEMS
• TROPHIC LEVELS
• SPECIES DIVERSITY
SPECIES ABUNDANCE
• AGRICULTURAL ECOSYSTEMS
• YIELD
• BLIGHT

Figure 1. The total environment.

universe. These are too all-encompassing to treat in a comprehensive way. Therefore, subportions of the environment are usually selected for study since only by creating such partitions can any element be described easily.

MULTIMEDIA ASPECTS OF POLLUTION

When the environment is partitioned for study, we often fail to remember that many pollutants move from one media to another in a circular fashion as part of a natural geocycle or they are forced by the control action of men. Pollutant control programs must consider these interactions so as not to remove pollutants from the air, for example, only to put the waste into a stream or to dump it thoughtlessly on the land (Figure 2).

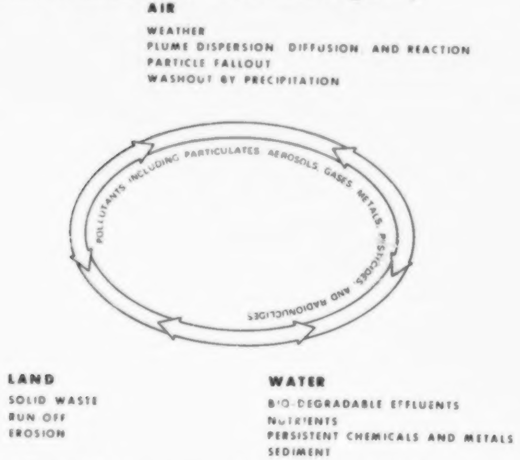
AIR
WEATHER
PLUME DISPERSION DIFFUSION AND REACTION
PARTICLE FALLOUT
WASHOUT BY PRECIPITATION
POLLUTANTS INCLUDING PARTICULATES AEROSOLS, GASES, METALS, PESTICIDES, AND RADIONUCLIDES
LAND
SOLID WASTE
RUN OFF
EROSION
WATER
BIO-DEGRADABLE EFFLUENTS
NUTRIENTS
PERSISTENT CHEMICALS AND METALS
SEDIMENT

Figure 2. Interaction of pollutants with the three environmental phases.

We live in a closed system and we can safely conclude that entorpy is ever increasing. This leads to a seemingly natural conclusion that we cannot eliminate pollution, and that our chosen actions result from considering the pollutant side effects of many alternatives and then selecting the action having the least effective form of pollution in the least dangerous media. Are we then faced with a situation where the effectiveness of our control technology will systematically fall behind because of population growth and industrialization?

The situation so depicted is not hopeless. We can learn to live in a polluted world. We will have breakthrough in technology; but, more important, we can slow down and even reverse the process. Some of the options include, but are not limited to, product or process changes and energy demand curtailment. Information needed to guide these policy decisions and to evaluate their effectiveness is provided by environmental monitoring systems.

MONITORING PURPOSES

We see at least four basic types of monitoring systems currently in use (Figure 3).

1. A surveillance system for enforcement actions in support of compliance and regulatory activities; this tends to be a source monitoring system;
2. An administrative system using environmental data for planning, budgeting, and assessing the impact of control programs;
3. An ambient monitoring system measuring the status of the environment containing a baseline subsystem and an early warning subsystem. This early warning subsystem monitors short-lived phenomena or episode and trends;
4. Lastly, a research and scientific system aimed at supporting effects studies and mathematical modeling. This system supports research activities which are usually established on a specific problem basis, including the identification of new pollutants, the in-depth study of problem areas, and the establishment of cause-effect relationships.

A great number of variations and refinements can be conceived. We believe that the above taxonomy will be useful in the following discussion.

Data collected by means of monitoring programs provide the raw data translatable into valuable information for:

1. The continuing assessment of the effect of pollutants and pollution on man, the natural and the modified environment.
2. The detailed study of pollutant formation, interactions, synergism, and patterns.
3. The development, establishment, review, and enforcement of criteria, ambient standards, and industry performance standards.
4. The evaluation of the effectiveness of adopted control procedures and preventive measures (control devices, institutional modifications, monies, etc.).
5. Planning resources used and product and process changes in order to minimize environmental impact.
6. Defining the need, direction, and intensity of future research programs.

CHARACTERISTICS OF MONITORING SYSTEMS

In spite of the fact that we have identified at least four types of monitoring systems, the tendency is to use similar instrumentation, techniques, and procedures in all cases. The result is that the objective of none of these

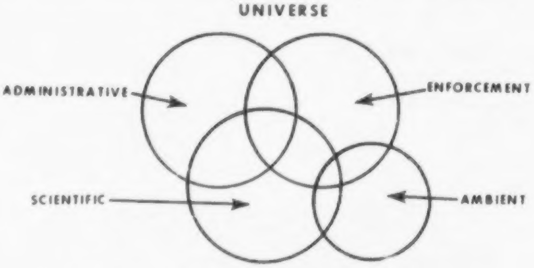

Figure 3. Overlap in monitoring systems.

ATTRIBUTES / SYSTEM	GRID SIZE RESOLUTION OR AREA COVERAGE	ORIENTATION	ACCURACY	COVERAGE (SPACE-TIME)	DURATION	RESPONSE
SCIENTIFIC	SMALL	GRADIENT	MAX	SPECIFIC	SHORT TERM	LONG
ADMINISTRATIVE	LARGE	AMBIENT	MIN	SYSTEMATIC	LONG TERM	IN-BETWEEN
ENFORCEMENT	LOCALIZED	SOURCE	MED	BIASED	SHORT TERM	SHORT
AMBIENT	MEDIUM	AMBIENT	MED	SYSTEMATIC	SHORT & LONG TERM	INTERMEDIATE

Figure 4. Characteristics of monitoring systems.

monitoring programs is satisfied in an optimal fashion. Figure 4 shows some important attributes for each of the four types of monitoring systems previously defined. The idea is not to provide a comparative analysis of the different systems, but to convey the wide range of attributes and the far reaching consequences of such requirements.

THE MONITORING PROCESS

Figure 5 identifies some important considerations at each step of the monitoring process; from the original concept to the end use of the information obtained. The attempt is not to provide a catalog or a check list, even though this would be a worthwhile project, but rather to indicate that a dynamic re-evaluation of each and every monitoring system, network, and project is called for in the light of the concepts identified in Figure 5.

MEDIA AND POLLUTANT EFFECTS

Media and pollutants, because of their varying characteristics, often define to a large extent the monitoring concepts selected and the instrumentation used, as well as the method of data analysis and presentation.

For example, Figure 6, fluid media move at varying speeds and are at least three dimensional. The velocity, temperature, and natural or induced stratification of the fluid seems to collaborate closely in inhibiting the attempts of the investigator to collect a meaningful sample. The area sustained by the sensor is an ill defined space in terms of volume and boundary. This condition frequently exists to the point of rendering analysis technically impossible.

The environment or the presence (known or unknown) of modifying factors including chemical and biological actions and reactions in a sample are especially relevant. This is particularly true in the case of integrated or grab samples. The presence of texture is an additional complicating variable.

Obviously, the measurement of rare populations, trace pollutant, or extreme values must be approached in a different manner than the ubiquitous pollutants which have more or less constant concentration values that lie in the middle of the operating range of the measuring device.

The monitoring network designer must surmount the difficulties imposed by the pollutant and media characteristics before the network can become operational and provide data.

SYSTEM QUALITY ASSURANCE CONSIDERATIONS

We have accumulated and computerized vast stores of environmental measurements. Environmental monitoring networks are growing as rapidly as pollution itself. Still,

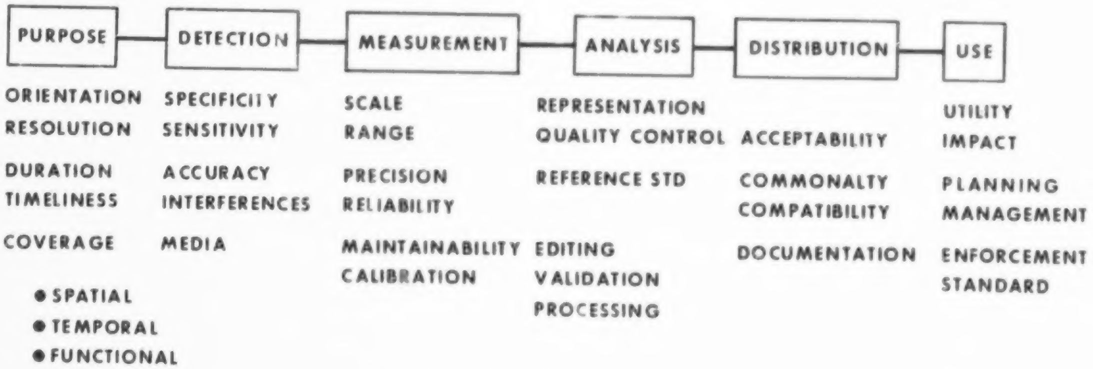
PURPOSE
DETECTION
MEASUREMENT
ANALYSIS
DISTRIBUTION
USE
ORIENTATION
RESOLUTION
DURATION
TIMELINESS
COVERAGE
• SPATIAL
• TEMPORAL
• FUNCTIONAL
SPECIFICITY
SENSITIVITY
ACCURACY
INTERFERENCES
MEDIA
SCALE
RANGE
PRECISION
RELIABILITY
MAINTAINABILITY
CALIBRATION
REPRESENTATION
QUALITY CONTROL
REFERENCE STD
EDITING
VALIDATION
PROCESSING
ACCEPTABILITY
COMMONALTY
COMPATIBILITY
DOCUMENTATION
UTILITY
IMPACT
PLANNING
MANAGEMENT
ENFORCEMENT
STANDARD

Figure 5. The monitoring process.

MEDIA	OBSERVATIONS
FLUIDS AIR WATER	STAGNANT/TURBITY/DEPTH/LOW FLOW
SOLID WASTE	DECAY-BACTERIA/LEACHING
SOIL/LAND	DEPTH/VEGETATION EFFECT/MATRIX/TEXTURE
POLLUTANT	OBSERVATIONS
METALS	RARE OCCURRENCE
PARTICULATE	SIZE/REACTIVITY
SO_2	RANGE OF CONCENTRATION

Figure 6. Media and pollutants define the monitoring system to be selected.

when we review our achievement (as scientists) in the field of monitoring, we are left unsatisfied with the result.

We venture to diagnose that a lack of systems approach to data acquisition and verification is at the root of our problems. Figure 7 is an attempt at introducing order in monitoring system design considerations.

Acquisition

Siting knowledge is one of the limiting factors in monitoring systems. If the accuracy desired and the range of the parameters are known, it is easy to estimate the required number of stations per unit area. The technique usually used is an inverse t-test. Unfortunately, findings from such studies have shown that the number of stations required is usually beyond economic and logistic feasibility. Mobile and/or moveable stations appear to be a method, with some loss of information, to increase the virtual number of stations almost infinitely.

The grid size or the interstation distance can be fine or large. Equally important, the grid can be systematic, that is every point of a virtual projected lattice is occupied by a station, or it can be totally random or biased to measure a specific source or a specific stream localized in space and time. Systematic sampling can be through a uniform or exhaustive enumerative approach, or it can use the transect approach.

Rules of thumb are available to assist in the location of sampling stations in terms of height above a fixed level (example, sea level, ground, etc.) as well as for avoiding the effects of interferences (man-made structure, lake, source). Unfortunately, selection of sampling station siting has been in the past dictated by the availability of specialized facilities. For instance, it is not known to this day how many air quality monitoring stations located on flat rooftop fire stations essentially record a carbon monoxide time series generated by

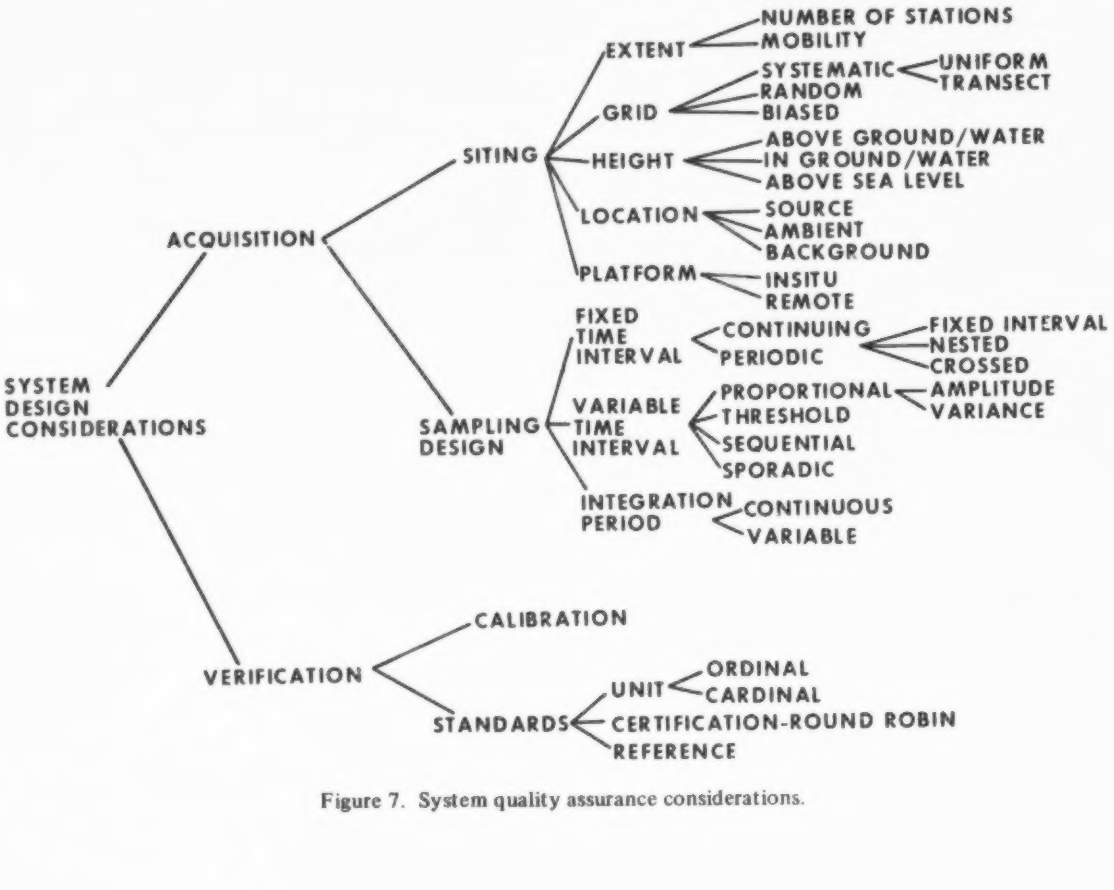
NUMBER OF STATIONS
MOBILITY
EXTENT
SYSTEMATIC
UNIFORM
TRANSECT
RANDOM
GRID
BIASED
ABOVE GROUND/WATER
SITING
HEIGHT
IN GROUND/WATER
ABOVE SEA LEVEL
SOURCE
LOCATION
AMBIENT
ACQUISITION
BACKGROUND
PLATFORM
INSITU
REMOTE
FIXED
TIME
INTERVAL
CONTINUING
PERIODIC
FIXED INTERVAL
NESTED
CROSSED
SYSTEM
DESIGN
CONSIDERATIONS
PROPORTIONAL
AMPLITUDE
VARIANCE
VARIABLE
TIME
INTERVAL
THRESHOLD
SAMPLING
DESIGN
SEQUENTIAL
SPORADIC
INTEGRATION
PERIOD
CONTINUOUS
VARIABLE
CALIBRATION
VERIFICATION
ORDINAL
UNIT
CARDINAL
STANDARDS
CERTIFICATION-ROUND ROBIN
REFERENCE

Figure 7. System quality assurance considerations.

trucks responding to fire alarms rather than the ambient carbon monoxide level.

The first order and generally the gross level criteria of location will usually be decided by the purpose of the monitoring program which include background, ambient or source monitoring. The more detailed question of measuring in-situ or from a remote site (whether a few feet away, a plane, a balloon, a satellite) is complicated by the fact that the distribution of pollution is nonuniform within the media. Remote sensing usually measures total burden, a column of pollutant (example, from the ground to the platform), but can also be used to take slice measurement across a volume.

Let us turn now to the sampling design. We see this concept being dominated by temporal aspects: time interval between measurement, averaging, or integration time and eventually reporting time. The interval between measurements can be fixed or variable. Fixed time intervals are commonly used by continuous and periodic sampling devices. A host of other options result when variable time intervals are considered. These sampling schemes, which are not currently in extensive use, offer many advantages in minimizing cost, storage, and data requirements. The idea of proportional sampling is to gear the sampling rate to such characteristics of the signal as variation, amplitude, or a combination thereof. Threshold or alarm sampling is based on the concept of collecting and transmitting data only if the signal monitored moves outside preset high or low boundaries. Sequential sampling consists of sampling a parameter or signal until some limit or condition is satisfied. The sporadic sampling category includes much of today's unplanned monitoring efforts.

It is our belief that the averaging time used in acquiring and reporting environmental data should be consistent with published standards. Except in the case of specialized research projects, the use of averaging time of less than one hour does not appear to be warranted by the gain in information.

Verification

Without a proper and systematic verification procedure, any monitoring program is without scientific value and probably inadequate for enforcement or administrative purposes. A satisfactory verification system is quite complex. We will cover only a few representative ideas here.

A standard or reference method should be operationally defined in terms of sampling procedures, equipment, sample handling, a laboratory testing (round robin), published and promulgated by a regulatory group. A need exists for a clear-cut procedure for certification of new standards and comparison with existing ones. A standard method should have, at least, the following characteristics:

- Utility
- Reliability
- Maintainability
- Low Cost
- Sensitivity
- Specificity

Environment parameters are given in a variety of units (example, ppm, $\mu g/m^3$, COH/1000 linear feet) and on ordinal, cardinal, and interval scales. If standardized units and scales cannot be set, and if it is desirable that they are, then standardized accurate and unambiguous methods by converting values among those units and scales which are employed are imperative. Some efforts have been started to standardize units. The rate at which these initial efforts are adopted must be accelerated and require the support of both individual governmental agencies and scientists engaged in research.

The previous chart (Figure 7) suggests many criteria by which monitoring programs should be evaluated during planning, development, and utilization phases. Consideration of the factors shown here is essential for effective design of monitoring systems.

DIMENSIONS REDUCTION

Because cost is often proportional to the number of stations, the number of analyses, and/or the number of computations, every attempt should be made in reducing dimensions. Cost considerations are not the only reasons why the dimension must be reduced. In order for policy makers to reach timely and effective decisions regarding alternative strategies, the monitoring program must be designed and operated subject to the ultimate system user's requirements. The size of the problem can be reduced during data collection, measurements, analyses, and presentations (Figure 8).

Collection

Reductions in the amount of data collected are possible within the areal and temporal aspects of collection. An example of an areal collection technique which rapidly provides the minimum amount of information required for a decision is illustrated by the topologically optimum water-sampling plan for rivers and streams described by W. E. Sharp. This is a procedure that optimizes the search for sources of newly discovered pollutants and will locate water quality monitoring stations according to a uniform plan. The centroid of a drainage network is located to divide the basin into two parts of equal magnitude. Samples are taken on both sides of the centroid and analyzed before taking the next sample so that one-half of the network could be rejected on the basis of the analysis. Similar sampling occurs around the centroids of remaining portions until the source is located.

The applicability of this technique for isolating pollutant sources in other media should be considered in the design of monitoring networks whose objective is enforcement of regulations. Modifications of the technique might be required to account for special

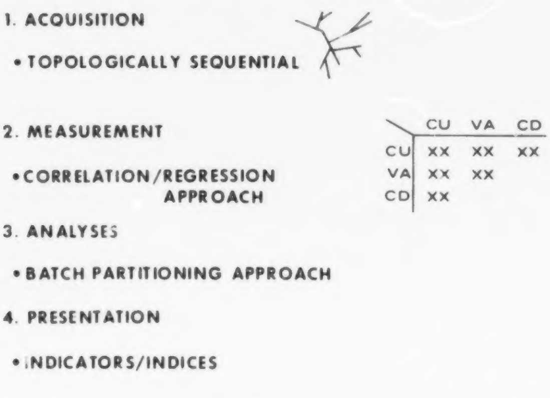

Figure 8. Dimension reduction.

segments of the monitor/pollutant/media/objective characteristics.

Examples of temporal data collection techniques which provide a sufficient number of samples to estimate pollutant concentrations within preset confidence limits are illustrated by analysis conducted by W. F. Hunt, Jr. and by the study of D. E. Phinney and J. E. Newman. These procedures specify the frequency of air monitoring necessary to characterize air pollution for a given time period and area to a given confidence interval. Conversely, the precision associated with preset sampling frequencies can be derived so the effectiveness of alternative plans under anticipated operational conditions can be examined.

Measurement

Another method of reducing the dimensionality of data while still obtaining maximum available information is demonstrated by employing the laten structure of correlations matrices to infer unmeasured pollutant concentrations. For example, based on the knowledge of cross correlations between pollutants or correlation with a third variable (example, population; number of cars), it is possible by measuring one pollutant of generally less than m to predict the concentration of other correlated pollutants by using such statistical methods as regression analysis.

Analysis

Various techniques exist for reducing the number of analyses needed to confirm, for example, the presence of a trace metal or to identify where it occurred. These techniques can generally be classified into group-testing methods. In these methods, analysis is made on a composite sample formed by combining a small portion of each sample. If a negative result is obtained, it can be concluded that none of the samples have the pollutant under investigation. If a positive result is obtained, then at least one of the samples contains the pollutant. A second analysis is then performed, usually on two composite subsamples. The process continues until a conclusion can be drawn for all original samples. Modifications to the batching method involve the number of composite subsamples formed and the number of original samples included in the individual composite. These modifications affect the rate at which a conclusion can be formed for the population of all original samples by determining the number of successive analysis which must be performed.

Presentation

To obtain a total view of our environment we are required, even forced, to conceive and measure a finite, but very large number, of pollutants or residuals associated with human activities. An equally lengthy list would be required to characterize the natural environment.

Reduction in the presentation dimensionality is necessitated by the vastness of the number of pollutants and the limited ability of the investigator to comprehend the net effect of simultaneous changes in individual pollutants.

Indicators have been developed in the past by employing simple deterministic models of variable relationships. A more powerful tactic would apply multivariate statistical methodology, such as principal component analysis and canonical correlation, to effectively reduce the dimensionality of the presentation manifold.

PURPOSE OF MONITORING SYSTEMS

If we need a taxonomy of monitoring systems, the most meaningful appears to be according to purpose. Three broad intents in monitoring programs are almost exclusively and exhaustively covered by a separation in normative, forecastive, and causative monitoring (Figure 9).

• NORMATIVE	CURRENT STATUS HISTORICAL TRENDS	BACKGROUND AMBIENT SOURCE
• FORECASTING	PREDICTION REACTION	POINT INTERVAL TREND
• CAUSATIVE	MECHANISMS INTERACTION	

Figure 9. Types of monitoring systems by purpose.

Normative can be redefined as descriptive. It either describes the current status or past historical trends and is used for background definition, ambient environmental qualification, and source characterization.

The causative or correlative monitoring concept attempts to reach fundamental issues involving mechanisms, interactions, and action reactions.

Forecastive monitoring is essentially a simultaneous projection and prediction. This kind of monitoring is often biological in essence using sentinel species to provide, because of their sensitivity, an alarm before the chemical/physical detectors can detect the effect or presence of environmental stressors. Forecastive monitoring can be further broken down according to the technique into statistical (prediction), biological (alarm), and physical/chemical (precursor).

CONCLUDING REMARKS

We would like to leave you with the following remarks extracted from the previous discussions:

1. Raw data are not information.
2. Pollution amount is not equivalent to concentration. We must measure both. Indeed we must learn to measure amount, concentration, effective fraction, size and characteristic distribution, reactivity, accumulation, reaction, synergism, etc.
3. Pollution monitoring is a study of extremes from source emission to epidemiological studies.
4. The ultimate environmental quality monitoring is an effect monitor. Ideally we need a personalized, portable, integrating, specific series of environmental monitors.
5. The quality of environmental monitoring data is defined by the weakest link in the total monitoring process.
6. The greatest needs and the greater requirement for improvement should be in concepts of monitoring as we have tried to show here today.

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SESSION V
ECONOMIC AND LEGAL ASPECTS

Chairman:

G. Strasser
Battelle's Columbus Laboratories

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ECONOMIC AND LEGAL ASPECTS

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I made a list of a few items to which I want to allude briefly. If we look at the so-called environmental situation today, and I avoid the term problems because of the makeup of the audience, we look at it from different points of view. The economists, the scientists, the people, the consumerists, and the advocates of consumerism, all have views of what the problems are. Perhaps it's fair to say that fundamentally what we are talking about when we discuss problems of the environment is an internalization of externalized costs. By this I mean many of our industrial products and services that we have been producing. The process itself has not absorbed the total cost of the activity but some of it has been externalized, either into our social or into our physical environment. As long as these social and physical sinks are not saturated, but perhaps limitless, there is no difficulty with such externalization. When they begin to saturate, the public gets frightfully excited about it. Then there is a drive to see just exactly how much is permissible to be discharged into the physical or into the social environment which creates disruption. I think, in the opinion of many, we have reached a point where there is too much concern about this balance. We have a movement today of how to improve our environment, and to a large degree this improvement will depend on how we can reintroduce into the original costs much of the externalized costs. This is much easier said than done. If all of a sudden we set standards that existed for the air or for the river 200 years ago, it is perhaps fair to say that the majority of our industries would be bankrupt overnight. Since much of what gets done today gets done with a de facto understanding of cost externalization, the real question that faces those who are concerned with the environment is not whether or not something has to be done about the situation. I believe most would agree that we should do something. The real question is twofold. How to do it? And, second, at what rate and in what manner should it be done? In the process we don't want to create more economic, social, and other disruptions than the good we would do by reversing this environmental trend. The things that have happened and evolved during decades, if not centuries, won't be re-written overnight. Therefore, the real trick is how to evolve the right mechanisms, the right legal and other ancillary processes which will allow us, in an expeditious way or manner to correct the situation.

There are a number of intriguing anecdotes about the difficulties of people who have tried to right some of these wrongs. I'm sure everybody in this audience is familiar with the Food and Drug Administration and with Dr. Herbert Ley who used to be its Director. I very vividly recall a testimony that he gave about three years ago in front of the Dario subcommittee. H said we set standards not based on physiological consequences as we should, but based on what our chemists, who are getting smarter and smarter by the year, can do in terms of detecting smaller and smaller trace elements in everything. If this trend is allowed to continue, he said, pretty soon we will find everything in everything and we will not be able to eat anything. He emphasized we should be trying to find a proper cause and effect relationship between what we do and what its causes are; we should differentiate between the risks that we as a government impose upon the population, which the population can do very little about, and the risks that people assume on their own. In the former category would be foodstuff that people have to eat. This is, so to speak, the government imposed risk. On the other hand, if you want to go skiing in the Alps, and break your leg, that may have a greater risk involved, but that's a personally selected risk.

During the era when there was a great deal of concern about mercury in tuna, I was at OST. We all had our assignments, and my neighbor got the assignment of answering phone calls which went like this: What is OST doing about mercury in tuna? Those of you in the government can appreciate a flood of calls like that from laymen. My neighbor at the office could take it only so long. After a while he said: We bind up all the tuna and are in the business of making thermometers. The job to answer tuna questions was reassigned to someone else the following day.

As you can see, many things are happening in trying to make this transition. I could rattle off a number of other things of which you are most familiar, such as the National Environmental Policy Act of 1969. I'm sure there is not a single individual in this room who doesn't know about this and about the Environmental Impact Analyses and the Environmental Impact Statement. Some say it is a new thing. Others asked what else is new under the sun? We have been doing some of this before. To what extent either of these statements is true I'm not prepared to say. Some of you probably know about a new law that was signed by the President two weeks ago – the Technology Assessment Act of 1972. This Technology Assessment Act is very intriguing because there are a great many commonalities – the subjects overlap almost 90 percent the concerns of the National Environmental Policy Act of 1969.

Just out of sheer conincidence I cam across something which I would like to share with you. It is an act, and I quote slightly paraphrased, which says every industrial plant shall use the best practicable means of preventing the discharge into the atmosphere of noxious gases and other noxious effluents arising from their work or of rendering such effluents harmless when discharged. Which of our two acts do you think this comes from? I'm not asking for an answer. I want to tell you that this is an English act, dated 1863, and the Preamble is slightly paraphrased. An act for the more effectual disposal of industrial wastes. Where it is expedient to provide for the better disposal of industrial wastes, be it enacted by the Queen's most excellent majesty, by and with the advice and consent of the lords, spiritual and temporal and common in the present Parliament assembled, and by the authority of the same that follows. The point I'm trying to make is that a lot of people have been grappling with problems like this, and nothing is new under the sun. The big difference between what has happened in the past and what is happening now is that we have saturated these things more than we saturated them in the past, and the leverage that technology permits us to exercise is much greater than it was in Queen Victoria's time. Therefore, if we do some good it could be much more than what we could do in the olden days. But if we foul up something, we can do a much better job of that too. So it's sort of important to try to do something about it in a systematic way without bankrupting ourselves in the process. This leads me to say that in doing all this I think it's imperative that the technical people and the engineers, who are so concerned with numbers and close-form solutions, whenever possible quote close-form second order, partial differential equations and operations research.

I'd be the last one to knock these subjects, because I've been making my living at them for a long time. But it's clear that other considerations have to enter into our deliberations. Nowadays things are not as easily modelable or simulatable as they have been. You really have to see new institutional frameworks and ways in which we can come to grips with the problems facing us, even though the roots of many of them date back to 1863 or before. In my opinion it would be nice if technical people would get a better perspective about the historical, legal, traditional, and other constraints within which these problems can be solved. And just to show that I don't discriminate against the technical people, I would also dearly like to have social scientists be made to take courses like calculus appreciation. Then the discussion of multidisciplinary problems, a first and second derivitive, and saturation curves and expedentials wouldn't come to them like the rediscovery of the wheel. There are a lot of things that we can do as we approach these problems in an interdisciplinary fashion. We must bring the practitioners up to speed by giving them some contacts and background that they lack due to the kind of education they receive. This background is imperative if they are to work jointly in a constructive manner.

THE SOCIAL IMPLICATION OF CONTROLS

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May I begin by reading you a quote of Blackstone's which is said to have influenced the thinking of Alexander Hamilton in the Declaration of Independence and the U. S. Constitution.*

> The principal aim of society is to protect individuals in the enjoyment of those absolute rights which were vested in them by the immutable laws of nature; but which could not be preserved, in peace, without that mutual assistance and intercourse, which is gained by the institution of friendly and social communities. Hence it follows, that the first and primary end of human laws is to maintain and regulate these absolute rights of individuals.

Individual or group awareness of the rights of citizens to the enjoyment of living or the quality of life and the part that communities must take in assuring these rights to all is the basic philosophy of today's environmental groups.

We no longer live in a simple world where clean air, clean water, and uncrowded land can be taken for granted. The problems of an over-populated world need the cooperation of all of us – government, industry, and citizens. Each problem begins somewhere. That somewhere is usually directly traceable to the fact that there are more people needing more jobs to earn more money so that they can consume more and ultimately throw away more. This has become a natural, normal way of life for most of us. But maybe there has to be an end to the kind of consuming we have been doing, and this kind of growth in our communities. What might have been considered progress and prosperity a few years ago can today be recognized as degradation and a misplacement of values.

Industry tells us that consumers demand many items: high phosphate detergents for whiter clothes; throwaway bottles and cans; fancy packaging; lighter throwaway plastic containers, and many more. But in truth it is industry which has spoiled us by producing these and other products, and convincing us that we need them through Madison Avenue ads. However, there is a growing interest and awareness on the part of the buyer today of the problems that are a result of this convenient living and overindulgence. We, at Concern, believe that we may be seeing the beginning of a buyer revolution where concerned citizens are looking for a new market for products created with an awareness of environmental impact. We have dealt with this new market in our publications called Eco-Tips.

We have also tried to encourage re-use and recycling for two reasons: to reduce solid waste and to help preserve our resources. Instead of being consumers, we must really become users and re-users if we are to protect the world around us for future users. A well known, or well-quoted, statistic is that although the United States represents less than 6 percent of the world's total population, we consume half of the world's natural resources (each year). I am not an economist, nor are most of the consumers whom I represent, but it really doesn't take an economist to realize that there is a limit to production and consumption which can be called progress. If we use up our resources without trying to find ways to re-use or recover them, we may find ourselves and our children running out of world in which to live.

As a first, and perhaps a small, step, we at Concern have joined with many interested citizens in trying to encourage recycling of paper, glass, and aluminum through the formation of recycling centers. In almost every city of any size in the country today you will find housewives lugging their recyclable items to one of these centers. This is not the long-term answer. But if there is a real effort on the part of citizens to return some of our resources for recycling, there will be more of an effort on the part of industry and government to work out a better solution for overall long-term resource recovery.

There is evidence of industry effort. For instance, in the aluminum industry 10 cents a pound brought back almost a billion cans in 1971 and may bring back more than a billion and a half in 1972. This is a small percentage – about 12 percent in 1971 of the total aluminum cans which could be recycled. But when you think that the percentage has risen from 0 percent to 12 percent in the past few years, the increase is at least encouraging. And although the money involved is perhaps the prime motivation, we feel that this increase in reclamation is dependent to a large degree on citizen interest.

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*William H. Marvell, Man-Made Morals: Four Philosophies That Shaped America.

Because of the difference in the value of the resources used in both glass and paper, recovery on an economic basis does not show the same promise as aluminum. But in spite of this, both industries are recycling on a larger scale than ever before. And in both instances the desire of citizens to cooperate has sparked a greater industry effort.

If it's true, as a spokesman for Reynolds has stated, that large amounts of aluminum have been recovered, and even larger amounts expected to be recovered because of the 10 cents a pound reward, why, then, is there skepticism about whether consumers will return bottles and cans to recover a five cent deposit. If consumers demand the convenience of throwaway containers as industry has repeatedly told us, then not even the aluminum drive will succeed. We believe, however, that citizens today have two basic motives prompting their behavior: Both environmental and economic.

It may take 10 to 20 years, maybe longer, to fully apply the technology available for separation before disposal, thereby reclaiming a much larger proportion of our valuable metals and other resources. But with interim measures involving citizen awareness of the necessity for resource recovery, there will be more of an educated interest in improved solid waste disposal systems which are not dependent on the volunteer efforts of consumers.

Part of our job, as we see it, is to encourage people to think more, use less, re-use whenever possible, and handle the remainder with the least hazard to the environment.

We have not actively advocated government controls. However, we have certainly suggested that individuals or groups control and rethink their consumer appetites in many areas. We have done this only after long months of study and conferences with government and industry scientists well-known in each field, and other highly credible private and environmental groups. The most important part of our work is the education of the many thousands of people throughout the country who have written us because they want to know what they can do, how they can do it, and why.

We knew that detergents with a very high percentage of phosphates were the biggest selling detergents, and we knew that these detergents probably produced the whitest wash. However, we felt convinced that women in many parts of the country would respond favorably to the suggestion that they switch to a low phosphate detergent or soap if they were made aware of the concern of limnologists in and out of government for the premature aging of many bodies of water in our country and the part phosphorous was playing in this eutrification. Sales of high phosphate detergents probably did not go down, but the voice of the consumer was heard. Local legislation was enacted in several areas, and industry reacted with a reduction in phosphates. The recent announcement of Proctor & Gamble of a reduction to six percent phosphorous makes the response of the big three in the detergent industry unanimous. Perhaps for a long-term solution, a substitute which is neither harmful to the environment, nor to humans, will be found because of consumer interest and government and industry research.

In the plastics area, we have tried to inform the consumer of the solid waste disposal problems of pvc containers. We have also been concerned about the recycling capabilities of plastics. Because of the action of many consumer groups, such as ours, and the concern of the government, especially E.P.A., industry has responded with a search for substitutes and a continued search for the recycling possibilities of all plastics.

While we all realize that some pesticides are sometimes necessary, we have tired to steer the housewife and the gardener toward other, safer methods of pest control, using the less harmful pesticides only when absolutely necessary. We have done this both through our Eco-Tips and our calendar called The Living Garden which we co-sponsored with the Audubon Naturalist Society. This calendar makes suggestions month by month on how to garden without dangerous pesticides and sells well throughout the country.

We have also tried to encourage the use of returnable bottles. Judging from the state and local legislation, either pending or enacted, we are not alone in believing that a container that is returned for re-use or recycling is the only environmentally sound container.

In the larger cities, particularly on both coasts, it is not surprising that community groups and environmental groups are not willing to sit quietly by while inversions trap pollutants from automobiles and citizens are warned that outdoors is off limits to them. The Clean Air Act of 1970 became a law because of the pressure of social groups on Congress. The controls spelled out in this law for Detroit to meet by 1975 and 1976 are tough controls, and may have profound economic ramifications, but I can't believe there is anyone, even in Detroit, who doesn't realize that the mounting air pollution from automobiles is a real problem and one that must be solved. Aside from the tremendous job E.P.A. has to face in this exigency, community groups must also become involved. Lay citizens are not capable of suggesting alternatives to the internal combustion engine, or the type of catalyst to be used as an anti-pollution device, or how many parts per million of carbon monoxide or nitrogen oxide should be allowable in the air they breathe, but the same citizens must become more aware and better educated to the problem so that they can understand how to help implement the solutions as they come along. Concern has tried to make suggestions to the citizens on its mailing list. Because of the potential health hazards of lead, we have suggested the use of the lowest lead, lowest octane gas that can be used without an engine knock. We have urged the use of unleaded gas whenever possible and tried to explain why. We have been told that many people are having the anti-pollution devices which are now being installed on cars removed because their cars use more gas and do not run as smoothly. This attitude can best be discouraged by an understanding of the problems of automobile pollution.

Our next publication, which we expect to have ready to mail in January, will be devoted to energy. We will try to help consumers realize the need for a change in attitude toward a more intelligent and efficient use of energy. All energy costs will go up in the future. We hope this rise in price will cause people to rethink their energy needs. Large amounts of energy can be saved without any real sacrifice. To this end we will make suggestions for energy conservation in the fields of transportation, architectural design, home heating and cooling, household appliances, and commercial waste. As far as recycled materials are concerned, we will try to encourage an expansion of the market. There are, and will be, many inconveniences (and expenses) for all of us if we are to clean up our environment. But if government and industry, and research institutions such as Batelle, Midwest Research, and others will work together to try to find answers, it is necessary for citizen groups such as ours to become better educated and to encourage the active cooperation of individuals and communities.

Realizing that teamwork is necessary in order to accomplish environmental and social goals, we might think of this teamwork in terms of a football game. The citizen team has long been missing from the football field. We have had industry teams playing, government referees, and citizens sitting in the stands screaming about the calls. These citizens should either be on the field, or lose their right to scream about the calls. We are beginning to see more today of the citizens coming out of the stands and getting onto the playing field.

No one would argue that the road toward ultimate solutions is a long one. I don't think any one would argue that this would be a much longer road without community involvement. We, as dedicated environmentalists, undoubtedly will stumble a little along the way to finding the long-term answers we are seeking. We feel an urgency to find well-thought out "Now" answers until technology is available for the long-term solutions. But there must be steps taken now by all of us, whether they be individual steps such as careful, selective buying, intelligent use and re-use, and thoughtful disposal, or group steps, such as an active interest in local legislation for pollution control and bond issues to support new technological advances for water treatment or solid waste disposal systems.

The worst thing that could happen for all of us, and our children, is to try to live with problems that vitally affect us, rather than trying to work together to do something about them.

HOW MUCH RECYCLING IS ENOUGH?

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INTRODUCTION

When people think of spaceship earth, they generally think of a closed economic system. Except for solar energy, in the long run all the flows are recycled. The idea is attractive because it implies a kind of social immortality. Until the far-off day when something happens to the sun, there is no reason why human existence cannot go on generation after generation. Actual spaceships are not immortal, of course. Apollo's life-span was considerably less than a month; and from the first day vital stocks were depleted while satellites of garbage began to accumulate around the spaceship. There is some irony in the fact that the economies of primitive tribes approximated the concept of spaceship earth far more closely than the actual spaceship Apollo. And modern economies seem to be moving away from the conditions of spaceship earth to those of spaceship Apollo.

A simple structure of economic flows is illustrated in Figure 1. For a long-run steady state, flows to and from each sector must be equal. In a primitive economy the extractive flow G is small, hence the waste flows A and B, and there is little to distinguish environmental dumps from environmental sources. Natural processes (C) quickly transform economic wastes A and B to their pre-use forms. But in a modern economy natural recycling cannot keep up with the production and discard of DDT, radioactive waste, fossil fuel combustion, packaging residuals, and the like. Not only cannot natural processes keep up with the increase in waste flows, but also the form of waste residuals is becoming less amenable to environmental processing. Flow C lags behind A and B and also extraction G.[†]

Modern economies are suffering from the twin problems of too much waste and too few raw materials. Greater recycling (more of C, D, E, and F) is often suggested as a solution to both problems. The question is how much recycling is just the right amount. A purist might be tempted to answer everything. But then are we to stop burning fossil fuel while waiting for new coal to form, and are we to stop using paint because its use is dissipative? A sophisticated version of spaceship earth is not to require that all sector flows be brought into balance, but only the costs of maintaining flows. Instead of closing down copper mines, in this version technology would be channeled and simulated sufficiently to offset the tendency toward rising costs as the better grade ores are depleted. Instead of a long-run steady state in flows, the sophisticated version recognizes that to achieve social immortality it is sufficient to maintain forever constant costs for service flows. At the opposite extreme of the purist (C = G) is the economist who might counsel us not to take any active policy toward recycling at all. Simply work to improve markets and then let the markets decide how much material of each type gets recycled.

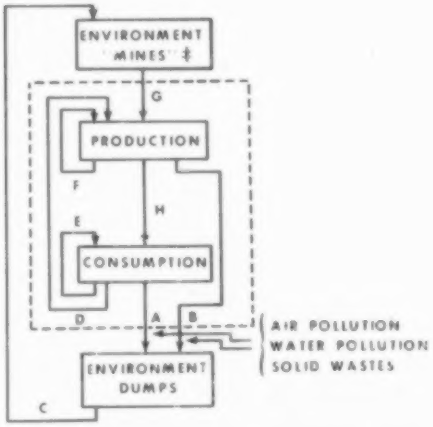

Figure 1. Simple schematic of environmental economic flows.

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[†] The dashed line is the boundary between the man-controlled and priced economy and the uncontrolled and unpriced environment.

[‡] "Mines" includes land for agriculture and forests.

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EFFICIENCY POINT OF VIEW ON RECYCLING

When an economist recommends the improvement of markets, he generally has a standard of market perfection in his mind. With perfect markets there are no monopolies; each firm is too small to influence market prices. Everyone is perfectly informed about market opportunities and product characteristics. Market transactions, as well as information, are costless. And, most important for us, all external costs are internalized. When a firm purchases labor inputs, the cost of labor is internal to the firm. But a firm's smoke emission is a cost as well, as it imposes burdens on those who receive it. If there is no smoke control, smoke emission is a cost external to the firm, and the incidence of cost falls outside the firm. If the firm pays for the smoke, by effluent taxes based on the damage to downwind receivers and by undertaking costly abatement activity, then the external cost of smoke emission is internalized.

There is an important theorem in economic theory which tells us that under the above conditions of market perfection the economy is welfare efficient. That is, there would be no way to rearrange economic inputs and production and distribution activities to make anyone in the present market better off without simultaneously making someone else worse off. It is difficult to see why society should be content with an inefficient economic allocation in which the lot of some can be improved without hurting others. In order to move closer to efficiency, certainly a desirable property, economists recommend steps that move us toward the conditions of perfect markets.

While recycling is not viewed as desirable in itself, steps toward the conditions of market perfection would increase the amount of recycling. In order to internalize costs, effluent fees or standards must be imposed upon the emission of air and water pollutants and disposal of solid waste. We can imagine toll booths set up on paths A and B with charges on the flows on the basis of downstream damage. The effects are obvious: Because of the increased cost of disposal, byproduct recovery becomes more economically attractive; instead of paying a penny a pound, say, to discard old newspapers, households would find the alternative of accumulating and recycling more attractive; in order to put off the final disposal fee, cars and other products would be designed for greater durability; products would become less material intensive (transistor over vacuum tube radios); and services would be favored over products, relative to the present situation. Flows D, E, and F would increase relative to A and B.

Since mining involves large external costs (acid mine drainage, tailings, etc., which we can visualize as flowing through B), internalization of costs would also favor recycling relative to G as well. However, some recycling activities are notoriously polluting so that internalization of costs would not encourage all forms of recycling.

It is easy to exaggerate the price changes caused by internalization of costs. Certainly internalization of costs will not drive us back to the 18 century, as some alarmists maintain. Economic theory strongly suggests that internalization of costs will substantially increase social well-being, not all of which is measured by GNP. Jerry Delson estimated that price increases in the coal-electric industry caused by internalization of costs would be in the range of 10 to 15 percent. (RFF study in process.)

From the point of view of economic efficiency, market perfection is important, not recycling per se, or durability, recoverability, or less material and energy intensive products. Whatever level of recycling that occured under perfect markets would be the right level. While the recommendation to internalize costs goes back to Pigou in the first part of the century, it is only recently that the recommendation has been put into practice. As the use of regulations, standards, and effluent fees becomes more widespread, we expect an increase in recycling and other forms of material and energy conservation. At the same time that extractive industries find themselves paying more of their external costs, the external costs themselves have been increasing. As we move from one percent to one-half percent copper ore the amount of solid waste to be disposed of doubles. And finally there is some evidence that the century-long trend of constant private costs of mineral extraction is changing toward increasing private costs. These three factors affecting resource extraction, an increasing fraction of external costs to be internalized, greater external costs, and growing private costs, all stimulate resource conservation (choke off G in favor of more D, E, and F).

As an economist I regret the last two factors which, if true, will diminish present and future welfare and show that we are beginning to lose the Malthusian race between diminishing returns to nature and technology; but I applaud the first factor which will increase our aggregate well-being though probably not the short run well-being of the mineral extractive industries.

MARKETS, EFFICIENCY, AND DEPLETION

Thus far the point of view of efficiency and perfect markets has had nothing to say about the second of our twin problems, that we are depleting our vital stocks of raw materials. When we use up tin and phosphates today and scatter them beyond reclamation, we pre-empt their use tomorrow. Foreclosure of the future's opportunity is a cost imposed upon the future, just as is bequeathing to the future high levels of mercury in ocean fish. Is depletion of tomorrow's resources an external cost in exactly the same way that unregulated pollution in the present is an external cost?

The answer is no. Individual firms have an incentive to take into account the costs of depletion imposed upon the future while there is no corresponding incentive, in the absence of regulation, disposal fees, or government specifications, to take into account the external costs of pollution in the present. If the owner of a mineral deposit believes that the future price is going to be bid up in response to the mineral's depletion and hence future scarcity, then the owner has an incentive to stretch out production. In the past incentive, while of great interest to economists, was probably very weak. Technology kept pace with Malthus, and with constant costs the speculative value of reservation was worthless. In addition, many deposits are in politically unstable areas overseas so that there is a powerful offsetting incentive to get it out before nationalization. Now, however, if the price trend is upward, for scarcity reasons, there may be more resource reservation due to speculation on future price increases. The point is that there is an asymmetry in ownership of material in the environment. In the environment at the top of the diagram, valuable materials are owned or are managed by profit-seeking firms. But in the environment at the bottom burdensome materials, pollutants, are disowned by these same firms, by means of smokestacks and outflow pipes.

So the twin problems of depletion and waste accumulation are not twin after all. The market fails where ownership fails. And by this standard many economists have taken ownership failure as a cue to advocate artificial markets of effluent fees and standards for wastes entering the environment, and the existence of ownership of resources as a cue to let the market decide how to allocate resource extraction over time.

Now let us suppose for a minute that somehow artificial markets have been created which effectively internalize the costs of waste disposal and the other conditions for perfect markets are more or less met. Is the market going to give the future a fair shake with respect to inter-temporal allocation of virgin resources? Is the market going to encourage us to gobble up the nonrenewable resources of this generation and leave scattered and contaminated residuals for the future to recycle as best it can? Perhaps it is fair for us to exploit the best deposits and leave the future with the remnants, for the future will be smarter, having better technology, and richer, at least in terms of GNP. Many will think it unfair.

In order to tell whether or not individual firms are motivated to practice sufficient resource reservation, we need a criterion to make the necessary comparisons between present and future well-being. Harold Hotelling, who developed the "theory of resource reservation," advocated along with many other economists a social criterion analogous to a firm's profit criterion. For each generation there should be defined a measure of well-being (welfare function), depending on individual preferences and market fulfillment of the preferences. Hotelling assumed that just as a firm is best off when it maximizes the present value of its profit stream, society is best off when it maximizes the discounted sum of social welfare measures. The criterion Hotelling proposed is an economics of the firm writ large. We will call it a present value welfare criterion (PVWC).

Many people find the discounting of future welfare repulsive because it seems to favor the present over the future. However, the PVWC is not inherently biased toward the present. If we are going to combine measures of welfare over time by addition, we have to discount the future to offset productivity in order to keep the future from being favored over the present. Suppose we took the PVWC with a zero discount rate: Instead of the present consuming a bushel of corn the criterion would instruct us to plant the corn so that the future could have two bushels. Furthermore there is a market tendency for a rate of discount to be equal to the productivity of capital; this in turn tends to equalize social welfare over time.

One reason for the popularity of the PVWC among economists is that it is a normative statement of what markets tend, more or less, to do by themselves. However, while the PVWC is not guilty of inherent bias toward the present, it does have a number of drawbacks. Perfect markets is an attractive objective intra-temporally because it leads to welfare efficiency for those in the present market. But perfect markets, which are somehow lined to the PVWC, do not guarantee welfare efficiency over the larger set of present and future people. In a market equilibrium the present is indiffernt between a little more investment and a little more consumption, but the future prefers more past investment to more past consumption. This non-matching of indifferences lays the basis for gains from trade, if trade were possible between generations. And the possibility of gains from trade means that the present equilibrium was not welfare efficient after all.

Linkage between present and future is a mechanism by which the future can influence the welfare of the present. For example, our present efforts at species preservation or wilderness preservation are more valuable to us if we believe that the next generation will increase its efforts at preservation. Diversity of species is an asset whose value continues over many generations. Our efforts at species preservation are not just for our generation, or the next, but for many generations. Thus our valuations of our efforts of preservation depend on our beliefs about future actions. Since all the traders, present and future, cannot bargain in a single room, there is no way for present markets to take into account these asset linkages. Consequently the market will provide too few of these assets whose value is linked over time. By the same argument the market will provide too many negatively valued assets whose disservices are linked over time.

On the other extreme from thinking that the PVWC inherently biases welfare toward the present, it is sometimes said that the PVWC, working through perfect markets, would maximize future welfare. The PVWC can only maximize one thing at a time, and the maximand is a sum of geometrically weighted welfare measures and not the welfare of any single period. The PVWC does not guarantee that future welfare will be as large as our own or even that enough resources wil be provided to sustain future existence.

Nor does the PVWC guarantee that allocations made by the present market are ones that we will be happy to live with tomorrow. It would be desirable to have a criterion which would allocate resources in such a way that if the next generation could change past allocation it would still keep the past as it was. The property of harmony is analogous to a regret-free life of an individual. "If I had a chance to live my life over I wouldn't change a single thing." The PVWC does not have the property of inter-temporal harmony.

In my judgment the prescription, "perfect the markets and let the markets decide" is distinctly less attractive in the inter-temporal case than in the intra-temporal case. In the intra-temporal case perfect markets would at least provide welfare efficiency. Not only that, but in the intra-temporal case efficiency can be separated from the problem of distribution of wealth. That is, for any given distribution of wealth market perfection leads to efficiency for those in the present market. We can, and do, alter the distribution of income and wealth through income taxes, while we independently recommend policy for market perfection by effluent taxes. But in the inter-temporal case it is impossible to separate the inter-temporal distribution of wealth from inter-temporal market allocations. Market allocations determine the distribution of aggregate wealth over generations. Because in the latter case efficiency cannot be separated from distribution, the PVWC is not so ethically neutral as the prescription for market perfection by internalizing enternal costs falling on the present.

Long-lived pollutants, such as radioactive wastes, DDT, and some heavy metals share the same ethical problem as conservation. We can think of these pollutants as negatively valued capital assets which give off streams of disservices as they depreciate. Many of these pollutants pose problems because their effects are unknown and we lose control of them once they get outside the economic sector. Emitted in very small concentrations they may accumulate in unforeseen ways to become highly toxic, or persist as backgrounds slowly raising the probability of cancer and other diseases.

Because these materials are sometimes very difficult to control once generated, the best control may sometimes be limitation of the generation. For example, cadmium is produced with every pound of zinc. Even processed zinc carries some cadmium with it, which gradually wears off into the environment. One way to control cadmium would be to recycle more zinc and mine less new zinc. That way less new cadmium would be introduced into the economic sector and ultimately less to the environment affecting man. Often, however, direct or indirect recycling will not be the answer to control of long-term hazardous materials. Control at the source and reduction of the source may sometimes be the best management of a toxic material.

As we saw, the perfect market prescription of effluent fees and standards said nothing directly about recycling, yet imposition of effluent taxes and standards would lead to more recycling. In the same way perfect markets say nothing directly about recycling, yet perfect markets with resource reservation due to speculation on future price increases should in theory lead to resource conservation. The point of view of efficiency treats the two problems of waste accumulation and depletion similarly; that is, as indirect effects rather than desirable goals per se. But, as mentioned, while the efficiency point of view is sufficient for the intra-temporal problem (pollution and waste accumulation) it is less satisfactory for the inter-temporal problem (inter-generational transfers of wealth from depletion and slow decaying pollutants). We may also wonder how effective is the market mechanism of resource reservation. Suppose a mining company can borrow or lend at eight to 10 percent but that it acts on an internal rate of discount at 18 to 22 percent. There is some evidence that such imperfections in the capital market are widespread. How much resource reservation will this company practice? Not much.

WHAT ABOUT SPACESHIP EARTH?

The point of view of efficiency and perfect markets has little to say about the future's right to existence. By the PVWC the future's right is a collection of desires which should be translated into willingnesses to pay and discounted to the present. This seems to be the wisdom of the PVWC. Yet we may ask who chose this criterion? It seems quite possible that if there were a vote between the PVWC and a criterion guaranteeing some form of social immortality, the latter would win. People tolerate many forms of market imperfection, monopolies and misleading advertizing, for example, but they make great sacrifices for their children and genetic lines.

Now let us assume that some form of social immortality is considered just and desirable. With this goal the cost of maintaining our present standard of living should not greatly increase, and perferably should decline, and the hazards of global catastrophe should in some sense be minimized. Then what should we do now, in the present? It seems clear that we should try to estimate various possible futures which result from present policy choices. We then choose those policy choices which lead to desirable future states. The procedure is a common one for macro-economic problems such as inflation and unemployment. For example, we decide that a six percent inflation is unacceptable, but a three percent inflation is acceptable. The goal seeming right and feasible, the money supply is then manipulated to achieve it.

One obvious policy instrument to move the economy toward a steady state of social immortality is the severance tax. Long-run population policies are perhaps even more crucial than material flow policies. The two policy areas are similar in that, for both, very gentle incentives can have enormous effect over a 200 to 300 year time horizon. A severance tax leads us toward spaceship earth in several ways. It raises the price of virgin material relative to secondary and hence encourages recycling. More important, in the longer run it stimuates technology to develop production processes that further take advantage of the relatively cheaper recycled materials. And of course severance taxes, in the long run, favor product durability and service intensive commodities over material intensive ones.

Severance taxes are like import tariffs in that they are collected at a small number of entry ports. They are far easier to collect than disposal taxes levied upon the final owner of a material. As states with anti-litter laws have found out, it is impossible to prevent surreptitious dumping. Schemes to collect disposal taxes at the last manufacturer have to provide for recycled content. And then definition and certification of recycled becomes a difficult problem, while the problem of surreptitious dumping remains with processors before the final manufacturer. Administrative costs of collecting a disposal tax are much higher at the final consumer (A) than at the first processor (G). It may be that the best place to collect a disposal tax is at G where it becomes a severance tax. To resolve the question one must weigh the reduction in administrative cost against the loss of efficiency from collecting the disposal tax too early.

Severance taxes are understandably unpleasant to mining companies, while they are something of a pipe dream to recycling companies. How can severance taxes come into being, one may ask, while depletion allowances, which are negative severance taxes, are so well entrenched? Yet in the near future people may take a harsher view toward tax policy which encourages depletion and helps transform spaceship earth into spaceship Apollo.

It is perhaps misleading to talk about specific resources as immutably nonrenewable with dates upon which each will run out. Perhaps the entire planet should be viewed as a single asset which managed in one way is renewable and managed in another way is nonrenewable. Economic theory tells us that even perfect present markets will provide us with too little of the time-linked renewable asset. The point is that the earth is an asset whose type can be changed; we have a choice as to which type of asset we want it to become. A hundred years from now the choice may no longer exist. We may have irrevocably transformed spaceship earth into a progressively more hazardous and time-limited spaceship Apollo.

HOW MUCH RECYCLING IS ENOUGH?

In terms of the first problem, the intra-generational one of waste accumulation, the proper amount of recycling is whatever amount that is induced by internalization of costs. In terms of the second problem, depletion and inter-generational transfers of wealth, it is much more difficult to ansser. A minimum which might appeal to many people is to provide enough incentives for recycling so that we do not foreclose the opportunity of a comfortable spaceship earth a hundred years from now.

LAW AND TRACE METALS

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INTRODUCTION

I have been asked to say a few words on the legal problems of trace metals. It has been a problem both in health and law for a long time; and, obviously, the discovery of the health effects had to precede any concern at law. Until the relationship between the presence of some particular metal within a product or process and a resultant disease has been established, there is no need for the attention of the law, or, at any rate until the advent of technology assessment concepts. This has been the prevailing view (1).

Confining myself to metals rather than embracing the larger aspect of trace elements, the presence of these has served many functions over the centuries and only slowly has there emerged any realization of hygienico-legal difficulties. I do not suggest that the difficulties of dealing with the entirety of the effects of all trace elements are generically different from the narrower issue of trace metals; but I do believe that how to cope with nitrates and the possibility of nitrate poisoning, carbon dioxide and the risk of the greenhouse effect, or industrial gases and solar irradiation in the atomsphere are far more major difficulties than any raised by trace metals (2). Hence my narrower scope.

The metals with which I am going to deal are lead, mercury, copper, zinc, beryllium, chrome, iron, cadmium, vanadium, nickel, and, while commonly not a metal, asbestos (3). Some of their side effects have long been known but only in recent ages have their dangers been commonly recognized. For example, the ancient Romans, lacking distilled alcohol, added lead salts to their wine in order to enjoy the resulting intoxication (4). Some attribute the fall of the Empire to the destruction of the intellectual capacity of the elite due to lead poisoning. During the Renaissance mercury was liberally used as a cure for venereal disease, with little regard for its less beneficent effects, and lead was employed by such beauties as Lucrezia Borgia for the dead-white face then so much admired (5). Copperous waters were considered healthful and were widely prescribed; and only recently have there been strong arguments against the popularity of "deliciously tasting" water heavy in iron. What was sought by one age has become a condition to be avoided by another. This is not to say that we are not right to seek such avoidance. It is only to observe that one could expect little prohibitory or corrective activity from the law as long as the above practices were common.

Furthermore, we have to recognize that ever more common economic activities have introduced into the receiving elements of air, water, and soil quantities of trace metals previously unknown on any except very territorially restricted scales. For example, a recent survey of earthworms near highways was conducted by the United States Fish and Wildlife Service (6). It was determined that levels of lead, zinc, nickel, and cadmium were sufficiently high to be fatal to birds consuming them. Zinc is in car oil and was found at all distances measured (maximum from the highway was 160 feet). At 50 ppm, zinc has been fatal to young pigs, but the lowest reading for the earthworms was 52.7 ppm. Lead is used in gasoline and was found in earthworms taken 10 feet from the highway to be 200 ppm, which is enough to kill mallard ducks eating such worms. Cadmium is emitted from tires and, while lethal to rats at 62 ppm, the heaviest concentration was 12.6 only. Nickel is used in oil and gasoline and was heaviest near the highway. In several instances, concentrations away from the highway were heavier than near it, which was explained as the result of water runoff. Clearly, the study revealed that the concentration of the auto on the modern highway introduces factors into the ecumene different than any known before and does so in a manner likely to have serious impact upon the ecology. This example does not directly affect human health, but similar illustrations with such a result could be found easily.

As a lawyer interested in the subject of trace metals, I have to point out that the interest divides between workmen's compensation law and the larger (and more hard to determine) law of general health and ecological effects. Both have been a long-standing interest of the

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law. As early as the 1880's, insurance to protect workers against the ill effects of their work was established in a few Continental countries and was urged by reformers (7). The common law in Anglo-American countries gave the worker no protection, in the absence of gross negligence by his employer, and gross negligence rarely was present within the customs of the time. The result was that, even though reformers began to push for statutes setting the conditions of work and ventilation in factories in England and the United States in the 1860's to protect the workers against bad air conditions (8), the laws to compensate workers for disease coming from those poor conditions did not begin to appear until the turn of the present century (9). As to generally atmospheric regulation, England set up an alkaline inspectorate in the mid-1870's; but it was not until the 1960's that either England or the United States came to have even somewhat effective air pollution control laws (10).

All of this, however, is history. Today there exist both federal and state laws on industrial hygiene, workers health and safety, workmen's compensation, and air and water pollution control that, directly or indirectly, are profoundly concerned with the consequences of trace metals in the environment as the result of economic activity (11). Some of them are of recent enactment, particularly at the federal level, and others are sufficiently old to have accumulated a large body of case law. But there is now enough to be able to select out pertinent materials relating to the subject, so that one can talk about both the problem and the law's attempted solution of it. Because of the nature of this paper, I shall use a distinction by the individual trace metals rather than by legal concepts in dealing with them. Beyond this, I have only my above caveat that the statutes and cases divide into the larger categories of concern with in-plant happenings and with effects upon the larger environment.

LEAD

The oldest metal for which serious side effects are known is lead. "Painter's colic" is a very old idiom and the law has dealt with it in the form of workmen's compensation awards since the establishment of that system of legal redress. The cases involving impairment of earning capacity, the aggravation of the disease, the size of the award, and so forth are numerous (12). I shall not discuss this aspect of the problem here but I shall, instead, move to considering the current public fears about lead: Namely lead-based paint and lead and lead alkyls in gasoline.

The use of lead in house paints has been regarded as a menace for the reason that its presence imparts a sweet taste to the paint flakes, which induces children to eat them. Examinations of slum children have shown large enough quantities of lead within their systems to adversely affect their intelligence or else to provide a dangerous situation if a prolonged fever should cause the body to attempt a mobilization of its resources. The result would be a drawing out of the stored up lead in one sudden rush (13).

Some have argued that this is an exaggeration. Not, they say, that lead is not a serious problem within inner city regions, but that banning it from house paint will solve no problems and will simply remove an effective, cheap fabric preserver of property from public availability. A recent study in the not-very urbanized city of Durham, North Carolina, showed that "lead yield is related to land use and the increased traffic density that corresponds to commercial development," so that "the yield of lead from the predominantly residential area W was one-half of that from the more commercially developed area N." Most of the lead was presumed to be contributed from surface wash and to be the product of exhausts of internal combustion engines of motor vehicles using leaded gasolines. The "annual yield of lead was determined to be 1,190 pounds per square mile per year" with "the more commercialized and densely urbanized portion of the basin studied yield[ing] lead at twice the rate of the less intensively developed portion of the basin, in direct proportion to the area of paved surfaces," thus indicating the danger to children in inner city areas (14).

Another reason why the removal of lead-based house paints will not solve problems for inner city children is indicated in a study by the child psychiatrist Reginald Lourie. Dr. Lourie's study shows that children suffering from lead ingestion are also victims of the symptom pica (L., magpie) which compels them to eat or at least put in their mouths all sorts of unsuitable substance, most commonly dirt which, considering lead levels in the inner city, will be high in lead. Psychiatrically these children suffer from neglect and the speediest, indeed the only effective, cure for this symptom is to induce the mother or the mother surrogate to show interest in the child. Nothing can reverse the damage done by what has been eaten, but at least the eating of unsuitable substances is stopped prospectively. Conditions such as these are hard to legislate about; but it helps explain why lead poisoning has not been found in many groups of children, even though lead-based paints are in their dwellings and lead-loaded soils are in their yards. These children are not pica sufferers because of a more fortunate parent-child relationship (15). Such psychiatric data does not justify the continued use of lead in interior paint; but it does help explain the unevenness of the problem and why the ban on lead-based paint will not provide a complete answer.

Congress temporized by enacting the Lead-Based Paint Prevention Act (16). Despite its ambitious name, its primary functions are to grant research aids for studying the effects of lead-based paints and for providing education for persons resident in areas where the use of lead-based paints poses a particular problem, as well as to assist them in seeking employment although damaged by the presence of such paint. The United States Public Health Service has issued a regulation as a notice of proposed rule making to ban lead-based paint in federal and federally assisted construction, which would have broad prospective effect (17). The United States Food and Drug Administration has proposed declaring certain heavy metal-containing paints and other surface coatings subject to a special labeling for child protection (18). They also propose to classify paints containing more than minute traces of lead as among "Banned Hazardous Substances" (19). The late Congressman Ryan proposed to ban the use of lead-based paint; but, to my knowledge, this has not been acted upon favorably (20). Ultimately, however, if the public pressure continues, lead-based house paint will be banned, at least for interior uses; persons using it illegally will be subject to criminal punishment; and, clearly, there will be pressure for public funds to be used to remove the accumulation of lead-based paints in housing interiors. All the above will be years in becoming effective. Once the image is established in the public mind of children having their mental faculties destroyed or impaired for life, by having eaten paint flakes while in their cribs, the politics of the image become very plain. And law is a consequence of politics.

Lead in gasoline is another common public concern today, and there is great pressure to compel refiners to remove it. Lead was introduced for its "anti-knock" properties to meet the needs of the higher pressure engines in the late 1920's and for this purpose has retained its popularity. The public has shown little interest in voluntarily using as alternatives the lead-free gasolines on the market, including many introduced in the past two years (21). Many say this is because they have not been adequately advertised and others say it is because they do not give the public the performance they want in gasoline. In any event, the pressure has been on for some time to ban the use of lead in gasoline.

In 1971 President Nixon, perturbed by the fact that 95 percent of the total lead emitted into the atmosphere comes from autos, proposed a tax on lead which would make leaded gasolines less competitive with the nonleaded variety (22). His then Secretary of the Treasury called lead "a clear and present danger" to the national health and backed a proposal for taxing it in gasoline (23). The President in his 1972 environmental message included a statement that federal regulatory measures must be taken in the future against the dangers of lead released into the environment (24). The Clean Air Act, as amended, had already stated that manufacturers of fuels and fuel additives could be required to register any additives used in fuel sold in interstate commerce (25). Clearly, this was meant to be preparatory to further legislative action since the registration in this act was solely for the purpose of gathering information and no regulatory activity was involved.

In February 1972 the Environmental Protection Administration issued a regulation on fuels and fuel additives relating to lead and phosphorus in motor vehicle gasoline (26). Basically it prescribed that there should be a decrease of such materials in gasoline and that by July 1, 1974 there be available on the market gasolines free of these substances, capable of being used in 1975 model cars (27). At about the same time, the EPA issued a paper in connection with leaded gasoline which was an analysis and summary of the medical and scientific evidence on the health hazards of air-borne lead (28). This was not a criteria document, but it was designed to underscore the reasons for the EPA's action. Recently, the EPA has also begun to become concerned with the quality of diesel fuel, and an across-the-board federal interest in all motor vehicle fuels is to be expected. The public concern does not show any signs of political abatement, despite the apparent lack of enthusiasm at the market level for lead-free gasolines. One can anticipate that there will be further regulations and statutes controlling the use of lead in fuels, indeed, probably eventually banning its use before the end of the present decade (29).

The public is continuously assailed by the fear of possibly harmful effects from lead. Recently, the importation of cookware and crockery from abroad, either made of a clay containing a high quantity of lead or with glazes having high quantities of lead and cadmium which are released either by heat or reaction with the organic substances in the dish, have attracted public attention. The warnings against both foreign and domestic ware that is dangerous under these conditions have been spread around and Senator Schweiker has introduced legislation to control the amount of lead and cadmium which may be released from ceramic or enamel dinnerware (30). Many persons have ceased to use Mexican pottery or peasant-ware imported from the Mediterranean because of these fears, even though any usage other than fairly regular would probably be safe. This merely underscores the fears with which the public continuously finds itself surrounded in relation to the metal lead in daily life.

MERCURY

Mercury is another substance high on the list of public fears. Litigation has been high in relation to this metal, notably the efforts of the State of Ohio to prevent its further dumping into waters draining into Lake Erie and to impose on previous dischargers the costs of cleanup (31). Environmental problems have affected the popularity of mercury and have very nearly halted United States production of it. In July 1965 the price was 725 dollars for a 76 pound flask. In May 1972 the price was 175 dollars, the lowest price for mercury since 1950. American use had dropped from 77,370 flasks in 1969 to approximately 48,000 in 1972. In 1970, there were 79 United States mines which sank to fewer than 30 by 1972. To meet expenses of production in the United States, the price must be somewhere between 225 and 250 dollars, in 1972 per flask. Changes in chlorine production have simply eliminated the use of mercury rather than seeking to control its use. World production of mercury, however, has dropped only slightly as the result of the American experience; and, conversely, the world's biggest producers, Spain and Italy, have upped production. Interestingly, according to the Wall Street Journal, the industry believes "nobody can afford research . . . to find nonpolluting uses for the metal," due to its present high production costs and low price (32).

The problems of mercury have acted to panic the public because of isolated horror cases. The use of mercury-dressed seeds either to make bread or to feed hogs has caused terrible harm to persons eating either the bread or the pork. In Japan, where residents of Minamata Bay eat mostly fish taken out of a very confined water body into which mercury wastes flow from a chemical plant, the harm has been extensive (33). "Mad Hatter's disease," because of its damage to mental process, nerves, and important bodily process, is one the public long has feared; and the pressure against mercury users will rise. Its use for seed dressings will probably be entirely eliminated, though this has used less than 3 percent of the domestic consumption of the metal. Labeling does not seem adequate to protect the rural agricultural laborer who has been the chief victim of the misuse of mercury-dressed seed. Modernization of techniques using mercury also seemed designed to eliminate it from the economy in anything like its present employ, even though as late as mid-1969 the United States Bureau of Mines insisted the use of mercury could be expected to increase indefinitely at up to 4-1/2 percent per year in industrialized nations. Paint manufacturers, although insisting they cause no problem, are considering eliminating mercury from their products (34).

The entire public attitude has changed radically since 1969 on the subject with the announcement of relatively high mercury contents in Lake Erie fish. "Minamata Bay sickness" loomed large in the public mind as a possibility in the United States. It has not been put at rest by subsequent investigations by paleoecologists which have shown mercury concentrations in museum fish specimens (35) and by studies of similar specimens to be in a probable decline since 1900 in the Unites States, possibly resulting from the lack of the use of soft coal. Nor have Americans been impressed by being told only heavy fish eaters from one source are most vulnerable, a condition of vulnerability not likely for the average American who buys from a national market and is not much of a fish eater anyway (assuming he is not on the Norman Jolliffe diet). Mercury is cumulative, as the old doctors who practiced calomel-and-castor-oil medicine knew; and this fact is cumulative in the public mind.

Because of this EPA has listed mercury along with asbestos and beryllium under the Clean Air Act as one of the three hazardous air substances (36). The ability of organisms to concentrate mercury is particularly noted in the regulations, and this is given as one of the reasons to be concerned with all mercury emitters, even those which might appear to be small. Anyone advising a corporation, therefore, would likely tell them, however small their use of mercury, to try to eliminate it altogether if possible. Why keep troublesome trifles around? Especially when they do not prove trifling in ecologic, industrial, or litigation costs.

ASBESTOS

A mineral which has created far less perturbation in the public mind, and yet is listed by the EPA as one of the three hazardous substances under the Clean Air Act, is asbestos. In medical literature, asbestosis, the disease associated with exposure to asbestos in the air, has been identified since 1924; but it was not until forty years later, when the New York Academy of Sciences held a conference on the biological effects of asbestos that the full impact of the mineral on public health was understood (37). It has been only since 1964, therefore, that the efforts have been mounted to control the use of asbestos from the point of view of protecting public health.

Asbestos is a mineral whose effect cuts across both workmen's compensation law (38) and the legal consequences of asbestos use as it affects members of the general public. Clearly the ones most endangered by asbestos are those whose employment regularly causes them to come into contact with it (39). However, regular usage need not be prolonged in order for the results to be serious and the effect may be so long delayed that the individual involved may have forgotten when he suffered exposure to the mineral. The Federal Occupational Health and Safety Act has lain down far tougher general rules than had previously prevailed in most states, and it is important today in the type of protection a worker may anticipate in his work conditions (40). Industrial hygiene legislation is designed to head off the need for workmen's compensation for industrially related illnesses. It removes the cause of the illness in the affected industrial processes or it requires that the worker be protected in his work situation from the effects of the work process with which his employment requires him to deal (41). The need for workmen's compensation indicates either an unawareness that a problem initially existed, a failure of the law to cope with the problem once it was discovered, or a technological impossibility of protecting the worker, coupled with a socio-economic decision that the process involved is too important to be banned because of the risks involved.

Outside of this, however, are the possible risks to the general public who are not exposed to asbestos in their employment situations (42). Commonly today in the construction of high-rise steel-frame buildings, asbestos is sprayed on the structure prior to closing it within its poured concrete envelopes and curtain walls. Before regulations were adopted (one of the toughest being New York City's ordinance which went into effect in February, 1972)(43), the effect was of a wintry snow scene. The tarpaulin coverings around the spraying process have proven totally inadequate in confining the asbestos, with the asbestos sifting out from under the canvas to blow loosely about the streets. It is normally both amosite and chrysotile asbestos, mixed with rock wool, glass fibres, and often plaster in order to make it fireproof, so that plaster dust today contains a heavy asbestos burden (44). What is the effect of the public being exposed to such a mixture in the air over the several weeks or months such construction takes, considering the fact some persons live as well as work in the vicinity of such construction?

This is not an easy question to answer. First of all, many Americans are mobile. That is, they may live near such a construction site, but their work, recreation, or other activity may cause them to be absent during the hours of construction activity. Others may be employed by a firm in the vicinity, but their conditions may cause them to be elsewhere or may take them in or out of the area. Furthermore, the increasing use of air conditioning acts to screen out from interior rooms the asbestos fibres. Very few Americans would get the exposure of South African laborers who both lived and worked near asbestos, lacked mobility, and hence were massively exposed. But even brief exposure to asbestos has sometimes been sufficient to initiate the disease (in one case, a six-week temporary job wrapping asbestos insulation around heating pipes triggered a mesothelioma fatal 23 years later) (45), and a no-exposure level for the general public would be best. After all, the best efforts will not prevent present generations from inhaling more asbestos than previous generations; and exposure of school children is particularly to be avoided since exposure at an early age produces poorer prognostications than at later ages.

Because of the impossiblity under current technology of sampling and measuring asbestos in the ambient air or in emission gases, the regulations of the EPA are expressed as requirements for the operation of specific control equipment or, where no control equipment is available, through prohibition of the use of asbestos (46). This is justified since the most dangerous asbestos particles are the submicroscopic and highly respirable variety which cannot be seen and whose presence may be unknown except as the individual may suffer a vague respiratory discomfort current with inhaling them (47). The consequence of such an approach is the emphasis that must be put upon the maintenance of the equipment, the adequacy of inspection, and the reaction of the legal machinery in its willingness to impose serious civil consequences upon equipment users who have failed to maintain it and whose failure has caused harm to individuals. The trouble with this last approach for effectiveness has two aspects: The individual either not knowing of his exposure or else not remembering or relating the exposure to the harm (said unawareness extending to his physician in terms of diagnosis) and the time lag between exposure and onset of the disease producing burdens of proof (48).

Americans are not a maintenance prone culture. Any system which puts its reliance in maintenance of an equipment system and bureaucratic inspection to keep the maintainers up to minimal standard is a system that is in for more failures than successes, if previous experience in other areas is a guide. Further, many of the contractors who work with asbestos are often the sort of undercapitalized, transient, indifferent entrepreneurs most likely to become scofflaws. The result is that the public risk from asbestos is likely to remain high until technology gets much better.

BERYLLIUM

The third hazardous air pollutant nationally singled out by the EPA under the Clean Air Act is beryllium. Industry long resisted the allegation that the use of beryllium in industrial processes could be productive of any long-term adverse effect leading to permanently debilitating illness. I recall observing, in the mid-1960's in northeastern Pennsylvania, a series of workmen's compensation hearings before a Commonwealth examiner in which employers conceded the cause of "Black Lung." But they vigorously resisted the imputation that the claims made for compensation for illness imputed to beryllium were allowable on the basis of the innocence of the mineral. For this reason, the courts allowed counsel for claimants to introduce into evidence, through the medium of hypothetical questions put to experts called by the claimant, whether a "conference of chemists and medical men had made any definite finding that beryllium was the sole cause of berylliosis." By the end of the decade this was a recognized illness for purposes of compensation under workmen's compensation laws (49).

The danger to the public was harder to establish, but it was finally determined that those residing near plants employing beryllium were in considerable danger. Indeed, as industrial hygiene improved within the plants, their dangers were probably greater than the workers. This is not an unusual phenomenon. Once the cause of an industrial illness is established, the insurance carrier of the employer becomes insistent upon alterations in industrial processes to mitigate extent of liability. Also the chances go up markedly for an employer, who refuses to respond to this pressure, to be liable for the far greater coverage of gross negligence or reckless and wanton misconduct under the common law of tort. The result is better conditions for the workers than prevail for the residents living in houses within several hundred feet of the plant.

The "known major sources of beryllium are extraction plants, machine shops and foundries handling beryllium or beryllium-containing alloys, ceramic plants using beryllium, rocket propellants containing beryllium, and incinerators burning beryllium-containing waste" (50). Because of the value of beryllium to harden substances to which it is added, its presence is common and likely to increase so that the above list is one that indicates fairly common contact with the general public. It indicates further some difficulty in enforcing any laws designed to protect the public or, if protection fails, to guarantee the person hurt a financially responsible entity to be the respondent in any damage action. In the latter regard, it does very little good to make liability for harm clear when the one liable is not capable of fiscal responsibility.

LESSER TRACE METALS

Other trace metals are of sufficiently narrow impact, or their consequences up to this point sufficiently unknown, so to treat them individually would be unsupported by adequate legal materials. Chrome dust, for example, is a serious problem in industrial processes, but it has not been one that much affects the public at large by any deteriorating of the atmosphere. Nevertheless, the Federal Occupational Health and Safety Act has a table of air contaminants including chromium, copper, iron (oxides), lead compounds, nickel, tin, zinc compounds, and others (51). One of the problems is the sharp increase in the use of certain trace metals in industrial processes which were unknown until very recently. For example, vanadium is now used in 18 compounds of itself in a wide variety of commercial processes (52). What is the effect of it? People have always had traces of vanadium in their systems but now it is increasing. What this means is simply not known medically and will not be until more experience is accumulated — experience which could be good or bad.

Most of these trace metals are included for purposes of legal and public concern under the rubric of "toxic substance," which of course is a far larger category than trace metals. In his 1971 Environmental Message, President Nixon proposed that the EPA be empowered to restrict the use or distribution of any substance which the EPA Administrator finds is a hazard to human health or the environment (53). This was a rather sweeping delegation of legislative powers, but analogous to what has happened in workmen's compensation legislation where the legislatures have stopped listing specific diseases or causes of disease and have gone over, instead, to merely indicating that all illness contracted in relation to employment is compensable. In his 1972 Environmental Message, the President proposed a Toxic Wastes Disposal Control Act which, under EPA supervision, would establish Federal guidelines for state programs to regulate the disposal of harmful wastes (54).

This type of concern at the chief executive level is correlated to concern at lower federal bureaucratic levels. The United States Bureau of Mines has a metallurgy program based upon the need to maximize the efficiency of metallic use and to minimize the quantities discharged as pollutants and wasted in the industrial process (55). The metals specifically mentioned are zinc and lead, but it would be equally applicable to others, particularly as it becomes evident that the bulk of supply for some metals in the future will be from recycling and reclaiming processes (56). The United States Department of Transportation has a Hazardous Materials Regulations Board which has issued an advance notice of proposed rule making which classifies certain hazardous materials on the basis of their health hazards; and these must include at least some of the trace metals (57). The Federal Council on Environmental Quality issued in April 1971 a booklet on toxic substances, pointing out their dangers and urging measures be taken to control the harmful side effects in their careless employment. Other examples could be pointed out in the federal structure of similar import since, once interest is high in the executive, judicial, and legislative branches of the government, it is evident that the administrators must indicate a zeal at least as significant as shown by those who generate the basic decisions, statutes, or orders within which the daily routines of public administration must be carried on (58). Whatever their historic inadequacies, it is the administrators who properly belong in the front line of the public's defense against the sort of risks posed by trace metals in the environment.

The law, as is to be expected from a discipline responding to outside pressures, has many avenues to resolving similar problems. Its relations with trace metals are no different in this respect. Just as one would look in the indices under "toxic materials" as well as atmospheric pollution, water waste control, or the names of the individual metals themselves, so also would one consider the heading "hazardous substances" or "dangerous properties of industrial materials" or similar language which occurred at some time to those pushing for a legal response to a health or environmental challenge. Often the legislative response is a narrow one, as in the Hazardous Substances Act, which does not cover the raw materials from which household products or toys are made (59), or in the old Water Pollution Control Act which authorized the President to designate hazardous substances and to recommend methods for their removal from the water (60). Anyone doing research in this area must consider such statutes as these if he is to cast his legal investigative net wide enough to be sufficient. Too narrow a point of inquiry will not cut an aperture wide enough to be useful.

CONCLUSIONS

Indeed, perhaps this paper suffers from this very narrowness against which I warn. As I said at the beginning, trace metals are generic in their problems to all situations in which some small quantity is discharged into the environment by an economic activity. In this case, environment includes air, water, soil, and the living cells, which, paradoxically, must count in the cells of what Claude Bernard called the "interior milieu" of humankind. Probably it is impossible in this situation to make any final separation of issues of human health and environmental fitness. For this reason, at one time, both public health and environmental law were so close as to be the same; and only the growing complexity of each, acting to prevent any one scholar from mastering them, has forced their separation one from the other.

In any comments on trace metals and the law, there is an interlocking of workmen's compensation, industrial hygiene, and environmental protection that makes it very difficult to steer safely through. Probably, from the lawyer's viewpoint, the subject trace metals, or even trace substances, is one that is insufficiently legalistic in its conceptualization; and for lawyers such terms as negligence, reasonable risk, etc. would be easier to deal with. However, subjects do not agitate society in the language that they perturb lawyers. Often, therefore, it is necessary to address the problem in words that are clumsy to the lawyer but which express what is uppermost in the mind of the public. The risks of trace metals are among these. Clumsy as this paper is because of this fact, nevertheless I believe the effort was worth making, slight as the result may be.

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6. 4 CCH Clean Air and Water News, 629–630, September 28, 1972.
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10. Arvill, op. cit., 98–99.
11. An interesting survey is Cleaning Our Environment, a Report of the American Chemical Society, Subcommittee on Environmental Improvement, Committee on Chemistry and Public Affairs, 1969, especially 26, 128–131, and 176 for the presence of trace metals in air pollution, waste water renovation, and solid waste.
12. See West's Key Numbers, Workmen's Compensation, 527 (inhalation of fumes, gas, and particles); 538 (lung diseases); and 549 (occupational diseases in particular).
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23. 28 Cong. Q. Wkly Rep. 2254, (September 18, 1970).
24. BNA Environmental Reporter, 21:0429 (February 8, 1972).
25. 42 USCA sec. 1857f-6c, PL 91-604, and 81 Stat. 502, sec. 210. The Clean Air Act first passed in 1962 and its predecessor the Air Pollution Control Act in 1955. See 40 CFR Part 79, Subpart B, 36 F. R. 22419 (November 25, 1971).
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44. Ibid., 49.
45. Ibid., 47–48.
46. 40 CFR, Part I; 36 F. R. 23239 (December 7, 1971).
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